

*STUDIES OF INTERNAL ROTATION
IN 1,3,5-TRINEOPENTYLBENZENES
AND RELATED SYSTEMS*

SVEN ANDERSSON



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Abstract ¹³C and ²H relaxation time measurements and molecular mechanics calculations were used to study the internal rotation in 1,3,5-trineopentylbenzene. In general, good agreement between experimental and theoretical data was found. Series of neopentylbenzenes and 1,3,5-trineopentylbenzenes containing benzylic substituents were synthesised and studied by ¹³C DNMR band shape and molecular mechanics calculations. C_{sp}³-C_{sp}²(aryl) and C_{sp}³-C_{sp}³ rotations were studied, and the results are discussed in terms of possible initial and transition states. For the 1,3,5-trineopentylbenzene system the existence of different low temperature rotamers is discussed and compared with results from molecular mechanics calculations. From estimated C_{sp}³-C_{sp}²(aryl) barriers the relative size of the CH₃ group in relation to Cl and Br atoms was found to follow the order Cl<CH₃<Br. From C_{sp}³-C_{sp}³ barriers the order CH₃<Cl<Br was found. Groups with both steric and electronic effects were introduced into 1,3,5-trineopentylbenzene and other 1,3,5-trialkyl-substituted benzenes, which were studied by ¹H NMR band shape, ¹³C relaxation time measurements and molecular mechanics calculations. Theoretical results on hydrocarbons generally agree with experiment, but for oxygen-containing compounds differences are found due to overestimation of steric effects in relation to the delocalisation effect.			
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SVEN ANDERSSON

Organic Chemistry 2, The Lund Institute of Technology, Chemical Center,
Box 740, S-220 07 Lund 7, Sweden



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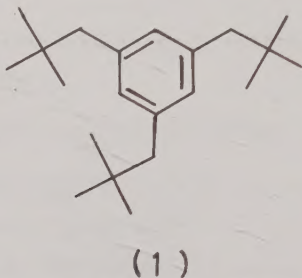


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INTRODUCTION

I.1 Background

1,3,5-Trineopentylbenzene (1) received a great deal of interest in the beginning of the 1970's as a subject for studies of kinetic deuterium isotope effects in aromatic substitution.¹⁻⁴



After the successful synthesis of 1,3,5-trineopentylbenzene (TNB) by Martinson *et al.*^{5,6}, many derivatives of this parent molecule were synthesised, and interest was focused on a number of them as subjects for NMR spectroscopic studies of internal rotation.⁷⁻¹⁸ Most of the derivatives hitherto studied by NMR methods have been TNB molecules substituted in the aromatic ring by halogen, alkyl, 1-hydroxyalkyl and acyl groups.⁴⁻¹¹

Carter and Nilsson *et al.*¹²⁻¹⁴ studied the restricted internal rotation of the neopentyl groups in TNB derivatives containing two similar or different halogens in the aromatic ring. Nilsson *et al.*¹⁵ studied the restricted internal rotation of the neopentyl groups in the trisubstituted compound 1,3-dibromo-5-nitroTNB by ¹H NMR spectroscopy. Later these phenomena were also studied by Nilsson and Drakenberg¹⁶ by ¹³C NMR spectroscopy. The results¹²⁻¹⁶ were discussed in terms of possible rotamers.

By use of dynamic ¹H and ¹³C NMR spectroscopy Nilsson *et al.*¹⁷ studied the influence of ring substituents on neopentyl barriers in TNB. The substituents were F, Cl, CH₃, Br, I and NO₂. Very large differences in measured barriers were found, and the results led to an attempt to correlate the relative

"effective sizes" of the substituents H, F, Cl, Br and I, placed in the TNB ring system.

Carter *et al.*¹⁸ studied the tri-substituted compounds 1,3,5-triR₃TNB (R= Cl, CH₃, Br), and interpreted the results in terms of different rotamers, at low temperature (Figure 1). In rotamer D all three t-butyl groups are on

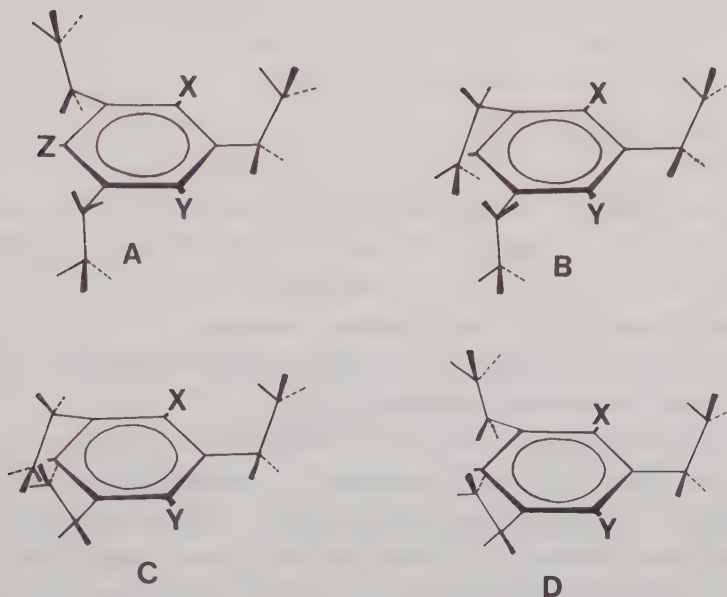


Figure 1. Possible rotamers in a 1,3,5-tri-substituted TNB. Note that the wedges and the full or dashed lines denote methylene protons or t-butyl methyl groups, as appropriate. The Z-substituent is omitted from rotamers B, C and D for the sake of clarity.

the same side of the ring plane, and in the other rotamers, A, B and C, two t-butyl groups are on one side of the ring plane and the third t-butyl group is on the other. In the case of X=Y=Z, rotamers A, B and C are indistinguishable by NMR. A ratio of rotamers D/(A + B + C) = 3 for 1,3,5-triBr₃TNB was estimated by Carter *et al.*¹⁸, and they suggested this as evidence for the existence of attractive steric effects among the neopentyl groups. The van der Waals forces between the t-butyl groups in the different rotamers of TNB may be either repulsive or attractive. In rotamer D there should be a maximum of

attractive forces among the t-butyl groups, and the net result is a better stabilisation of the initial state in this rotamer than in any of the rotamers A, B and C. This difference in initial state energies will thus lead to a predominance of rotamer D.

Carter and Stilbs¹⁹ made molecular mechanics calculations on the various rotamers of TNB, 2,4-dimethylTNB and 2,4,6-trimethylTNB. Their results provided theoretical support for the operation of attractive steric effects among the neopentyl groups and a predominance of rotamer D, being the most energetically favourable (by 3.8, 4.3 and ~ 6 kJmol⁻¹, respectively, for the compounds above).

I.2 Present study

This thesis begins with a study of the parent molecule TNB (chapter V). Only an upper limit for the barrier to internal rotation of the neopentyl groups had previously been estimated from ¹H NMR studies involving simulation of line-widths in 2-bromo-3,5-di-t-butylneopentylbenzene.¹⁷ ¹³C and ²H relaxation time measurements and theoretical molecular mechanics calculations were used here to study the internal rotation in TNB.

As nearly all TNB compounds studied earlier are ring-substituted TNB:s, benzylically substituted TNB:s seemed to be attractive objects for NMR studies. A literature survey showed that benzylically substituted mono-neopentylbenzenes have rarely been studied²⁰⁻²³, and therefore a more thorough study, involving ¹³C NMR spectroscopic measurements and theoretical molecular mechanics calculations, was undertaken (chapter VI). The TNB systems could then be more easily analysed by ¹³C and ¹⁹F NMR spectroscopic measurements and theoretical molecular mechanics calculations (chapter VII).

Finally, TNB systems with ring-substituents having both steric and electronic effects were studied (chapter IX). In connection with this work, other similarly substituted 1,3,5-trialkylbenzenes were studied. For this purpose ¹H NMR band shape analysis, ¹³C relaxation time measurements and molecular mechanics calculations were used.

II. THE DYNAMIC NMR METHOD

In this work, barriers to internal rotation were studied by the variable temperature NMR technique. Today this technique is very well established, and has been applied to a wide range of conformational problems.^{24,25} The variable temperature NMR method is suitable for studies of processes with free energies of activation in the range 20-120 kJmol⁻¹.

The processes studied in this work are: i) exchange of two groups of equivalent spin- $\frac{1}{2}$ nuclei (¹H or ¹³C) between two uncoupled sites with equal or unequal populations; ii) exchange of two groups of equivalent nuclei (¹H) between two coupled sites with equal populations (i.e. AB case); and iii) exchange of three equivalent nuclei (¹³C and ¹⁹F) among three uncoupled sites, of equal or unequal populations.

II.1 Band shape methods and measurements

The theory of exchange-broadened NMR spectra is based on the Bloch equations.²⁶ These equations have been developed by Gutowsky *et al.*²⁷⁻²⁹, Hahn and Maxwell³⁰ and McConnell³¹, and expressions for the case of exchange of two groups of equivalent nuclei between two uncoupled sites have been derived. Expressions suitable for calculations of the mean life time (τ) are given elsewhere.^{31,32}

The equations for exchange between two sites can be extended to cases involving exchange between more than two sites. Today elegant procedures for the solution of equations concerning exchange between many sites without couplings are readily carried out with available programs.^{25,33}

A general method for developing expressions in coupled systems has been presented by Kaplan.^{34,35} The method of Kaplan was further developed by Alexander and Johnson in a way which very much resembles the Hahn, Maxwell and McConnell treatment of the Bloch equations.³⁶⁻⁴⁰ Suitable expressions for exchange between two sites with coupling (i.e. AB cases) are thus common in the literature.^{32,41}

In most cases, the NMR spectra were recorded at at least 10 different temperatures. The mean life times (τ) were estimated from visual fitting of plotted spectra to the experimental ones.

The transverse relaxation time T_{21} is related to the width W_1 (Hz) at half-height of the peak unbroadened by exchange by equation (1).^{25,32}

$$T_{2i} = (\pi \cdot W_i)^{-1} \quad (1)$$

In all cases possible, T_2 was determined at both the high and low temperature limits for the exchanging signal and a reference signal (T_2^{ref}) originating from a nucleus in the same molecule and which is invariant with temperature. At intermediate temperatures, T_2 was interpolated by use of equation (2).^{42,43}

$$T_2^{-1} = (T_2^{\text{ref}})^{-1} + \pi \Delta\nu_{\text{corr}} \quad (2)$$

$\Delta\nu_{\text{corr}}$ is a correction factor and is assumed to vary linearly with temperature. In cases where only high (low) temperature data on T_2 and T_2^{ref} could be obtained, these values were extrapolated to low (high) temperatures. Equation (2) rests on the assumption that the linewidths of the reference signal and the NMR signal studied are equally affected by changes in solvent viscosity and magnetic homogeneity.

Determination of chemical shifts at temperatures where this parameter could not be estimated by band fitting was done by extrapolation from data below the coalescence temperature.

The ^1H NMR spectra used for band shape analysis were recorded on a JEOL MH 100 spectrometer equipped with a JNM-VT-3C temperature control unit, and on a Varian XL-100 spectrometer. The ^{13}C and ^{19}F spectra were recorded on the Varian XL-100 spectrometer operating at 25 MHz and in the Fourier transform mode for ^{13}C .

The temperature was measured by means of a copper constantan thermocouple, which was fixed near the receiver coil. The accuracy in these values has been shown^{13,17} to be better than $\pm 2^\circ\text{C}$ and is reproducible within $\pm 0.5^\circ\text{C}$.

Band shape analyses involving calculations of theoretical spectra for exchange between two sites were performed on a HP 9820A calculator equipped with a plotter. The calculations of spectra for exchange between many sites were performed on a UNIVAC 1108, equipped with a Calcomp plotter.

II.2 Evaluation of thermodynamic parameters

The mean life-times (τ) obtained from the band shape analyses are related to the first-order rate constant k by $k = \tau^{-1}$, and were used in conjunction with the Eyring equation (3) to calculate the free energy of activation ($\Delta G^\ddagger$) at

each temperature (T).⁴⁴

$$\Delta G^\ddagger = R T \ln 10 (10.32 + \log T \text{ k}^{-1}) \quad (3)$$

The relative statistical errors in estimated $\Delta G^\ddagger$ values were estimated by the approximate expression (4), which can be derived by analysis of equation (3).²⁵

$$(\sigma_{\Delta G^\ddagger} / \Delta G^\ddagger)^2 = [\ln 10 (10.32 + \log T \text{ k}^{-1})]^{-2} (\sigma_k / k)^2 + (\sigma_T / T)^2 \quad (4)$$

Here $\sigma_{\Delta G^\ddagger}$, σ_k and σ_T are the relative errors in $\Delta G^\ddagger$, rate constant and temperature, respectively.

The thermodynamic parameters enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) of activation were estimated for some compounds from a plot of the estimated $\Delta G^\ddagger$ values versus the temperature (T).²⁵

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \quad (5)$$

According to the Helmholtz equation (5), the $\Delta H^\ddagger$ and the $\Delta S^\ddagger$ values are found as the intercept and the slope of the curve, respectively. The errors in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ could be estimated from the plot of $\Delta G^\ddagger$ versus T when the error bars in $\Delta G^\ddagger$ were marked in the plot. The total uncertainty is thus represented by a rectangle. Two straight lines pivoting about the coalescence temperature and passing through the rectangle gave two different slopes and intercepts. The difference in these parameters was taken as the maximum error.⁴⁵

III. THE RELAXATION METHOD

Relaxation time measurements have proved to be very useful to study inter- and intramolecular motions in the liquid state and have been found suitable for processes with energies of activation from almost zero to 20 kJmol⁻¹.⁴⁶⁻⁵² In this thesis, two types of relaxation are dealt with: a) ¹³C-¹H dipolar relaxation and b) ²H quadrupolar relaxation, and these two types of relaxation and their measurement will be described later in chapters III.2 and III.3. By the use of appropriate calculation models, quantitative information about internal motions in molecules can be obtained from the relaxation data.

III.1 Mathematical models

The free diffusion model

Woessner has derived an expression for the dipolar contribution of the spin-lattice relaxation time in a system of two identical spins $I = \frac{1}{2}$.⁵³ This equation can be extended to systems involving many nuclei.⁵³

In the Woessner model, the motion is such that a spin-spin vector reorients internally about an axis which in turn may undergo random reorientation at a different rate (isotropic overall motion). The internal rotation is regarded as a diffusion process among a very large number of equilibrium steps.

Brevard, Kintzinger and Lehn have rewritten the Woessner equation in a more useful form (6).⁵⁴ Extremely rapid reorientation of the tumbling axis is assumed (extreme narrowing limit).⁴⁶

$$\tau_{\alpha} = A \tau_m + B [(\tau_m)^{-1} + (\tau_i)^{-1}]^{-1} + C [(\tau_m)^{-1} + 4 (\tau_i)^{-1}]^{-1} \quad (6)$$

$$A = \frac{1}{4} (3 \cos^2 \beta - 1)^2$$

$$B = \frac{3}{4} \sin^2 \beta$$

$$C = \frac{3}{4} \sin^4 \beta$$

τ_α , τ_m and τ_i are the effective local correlation time, the molecular correlation time and the internal correlation time, respectively. β is the angle between the internuclear vector and the preferred axis of rotation. For the case of ^{13}C relaxation,

$$\tau_\alpha^{-1} = \mu_0^2 (4\pi)^{-2} N_\alpha \gamma_C^2 \gamma_H^2 \hbar^2 r_\alpha^{-6} T_{1\alpha}$$

$$\tau_m^{-1} = \mu_0^2 (4\pi)^{-2} N_m \gamma_C^2 \gamma_H^2 \hbar^2 r_m^{-6} T_{1m}$$

$$\mu_0 (4\pi)^{-1} = 10^{-7} (\text{NA}^{-2})$$

Here N_α and N_m are the number of protons bound (with the bond lengths r_α and r_m) to the corresponding ^{13}C nuclei with the relaxation times $T_{1\alpha}$ and T_{1m} . γ_C and γ_H are the gyromagnetic ratios for the ^{13}C nucleus and the proton, respectively.⁵⁵

The restricted diffusion model

London and Avitabile have developed a model for restricted internal diffusion between two states superimposed on an overall isotropic diffusion motion. The model has been applied successfully to the ^{13}C spin lattice relaxation in macromolecules.⁵⁶

This model considers free internal diffusion over a restricted range (from $-\theta$ to $+\theta$) about an axis making an angle β with the relevant C-H relaxation vector. Overall molecular motion is assumed to be isotropic and a dipolar mechanism for the ^{13}C nuclei due to interaction with directly bonded protons is assumed to be dominant. The formula developed by London and Avitabile (7) relates the relaxation time ($T_{1\alpha}$) for a ^{13}C nuclei to spectral density terms, $J(\omega)$.⁵⁶ The spectral densities are calculated from an expression ($E(a,n)$) giving a matrix for the restricted motion.

$$T_{1\alpha}^{-1} = N_\alpha \gamma_C^2 \gamma_H^2 \hbar^2 (10 r_\alpha^6)^{-1} [J(\omega_C - \omega_H) + 3J(\omega_C) + 6J(\omega_C + \omega_H)] \quad (7)$$

$$J(\omega) = \sum_{a=-2}^2 \sum_{n=0}^{\infty} |d_{a0}(\beta)|^2 |E(a,n)|^2 \tau / (1 + \omega^2 \tau^2)$$

$$\tau = [6D_0 + n^2 \pi^2 D_i (4\theta^2)^{-1}]^{-1}$$

With $E(a,0) = \frac{\sin a\theta}{a\theta}$

$$E(a, n \neq 0) = 2^{-\frac{1}{2}} \left[\frac{\sin(a\theta - n\pi/2)}{a\theta - n\pi/2} + (-1)^n \frac{\sin(a\theta + n\pi/2)}{a\theta + n\pi/2} \right]$$

$$6D_o = \tau_m^{-1}$$

$$D_i = \tau_i^{-1}$$

D_o is the isotropic diffusion coefficient and D_i is the internal diffusion coefficient.⁵⁶ London and Avitabile have pointed out that the relation between D_i and τ_i is somewhat arbitrary, but I set $D_i = \tau_i^{-1}$ in accord with the convention used in the free diffusion model.^{45,51,52} θ in equation (7) is half the jumping angle (from $-\theta$ to $+\theta$), ω_C and ω_H are the resonance frequencies for the ^{13}C nucleus and the proton (radsec^{-1}). $D_{ao}(\beta)$ are the reduced second rank Wigner rotation matrices and are given elsewhere.⁵⁷ All other variables are as defined above for the free diffusion model.

The model of London and Avitabile has some limitations. Equation (7) is only valid for cases where changes in $N_\alpha T_1$ with θ are monotonic. For certain combinations of D_o ($\leq 10^6 \text{ s}^{-1}$), D_i (10^{10} s^{-1}) and θ (180°), equation (7) shows a non-monotonic behaviour, and the authors⁵⁶ also point out that application of the model to the analysis of internal motion for certain values of the parameters is suspect.

III.2 Measurements of ^{13}C relaxation times

The spin-lattice relaxation time (T_1) for a ^{13}C nucleus from which the protons have been decoupled by application of a noise modulated radiofrequency field can be divided into two main contributions (8).^{46-52,58}

$$T_1^{-1} = T_1^{\text{DD}}{}^{-1} + T_1^{\text{O}}{}^{-1} \quad (8)$$

The term T_1^{DD} is the contribution of dipole-dipole interactions with the protons, and the term T_1^{O} includes contributions from all other mechanisms, such as spin-rotation, chemical shift anisotropy and scalar spin lattice relaxation processes.^{46,47,49}

Separation of the two terms on the right hand side of equation (8) can be

accomplished by measurement of the nuclear Overhauser enhancement (NOE) factor n , which depends on the ratio of T_1^{DD} to T_1 (9):^{46,49-52,58,59}

$$\frac{T_1}{T_1^{DD}} = 2 \cdot n \frac{\gamma_C}{\gamma_H} \approx \frac{n}{2} \quad (9)$$

The NOE for a ^{13}C nucleus is the enhancement found for the ^{13}C resonance signal when the bound protons are decoupled by irradiation with a strong radio-frequency. The NOE:s can be determined in two ways. One way involves first recording the ^{13}C spectrum with wide band ^1H decoupling and then recording the ^{13}C spectrum without ^1H decoupling. The factor n can then be estimated (for each ^{13}C nucleus in the molecule) by dividing each individual peak integration in the continuously decoupled spectrum $I_Z(^{13}\text{C})$ by the corresponding peak integration in the uncoupled spectrum $I_O(^{13}\text{C})$, according to equation (10).^{46,49,51,52,58,59}

$$\frac{I_Z(^{13}\text{C})}{I_O(^{13}\text{C})} = 1 + n \quad (10)$$

A more refined method in measure NOE:s involves first determining the spectrum with continuous wide-band proton decoupling. Then a second spectrum is recorded by using pulse modulated wide-band proton decoupling such that the decoupler is gated on only during data acquisition periods, and during the remainder of the intervals the decoupler is gated off.^{46,51,60-63}

There are many methods for measuring ^{13}C spin-lattice relaxation times (T_1), utilizing continuous wave (CW) and pulse techniques.^{46,47,64} The method used here is called the inversion-recovery method, with Fourier transformation of the resulting free induction decays (IRFT).^{46,47} In the inversion-recovery method the sample is subjected to a series of pulse sequences of the type $(180^\circ - t - 90^\circ)_N$, where the waiting period t (between the 180° and the 90° pulses) is varied in successive experiments. The relaxation time (T_1) can then be estimated for each carbon nucleus from a plot of $\ln(S_\infty - S_t)$ versus t according to equation (11).^{46,47}

$$S_t = S_\infty (1 - 2e^{-t/T_1}) \quad (11)$$

S_{∞} is the signal intensity at equilibrium (proportional to the equilibrium magnetisation) and S_t is the signal intensity at time t , for the ^{13}C nuclei.

A more accurate way to estimate T_1 values, which was used here, is to make a three parameter fit to an exponential function with the S_t values. This method has been described in more detail by Mayne *et al.*⁶⁵ The error limits found from this evaluation of T_1 values are 3σ , where σ is the "marginal" standard deviation, as defined by Mayne *et al.*⁶⁵

The ^{13}C relaxation measurements were performed on a JEOL FX-60 and on a Varian XL-100 spectrometer operating at 15 and 25 MHz, respectively. The 90° pulse lengths were 13 μs and 50 μs for the FX-60 and XL-100 spectrometers, respectively, and the time between pulse sequences was $> 3 T_1$ in all cases.

III.3 Measurements of ^2H (quadrupole) relaxation times

For a nucleus with spin $I > \frac{1}{2}$, the quadrupole relaxation time (T_q) is related to a single correlation time (τ_q) under extreme narrowing conditions, by equation (12).^{46,47,66}

$$T_q^{-1} = \frac{3}{40} \frac{2I + 3}{I^2(2I-1)} \left(1 + \frac{\zeta^2}{3}\right) \left(\frac{e^2 Q q}{\hbar}\right)^2 \cdot \tau_q \quad (12)$$

Here q is the electric field gradient at the nucleus of quadrupole moment Q , e is the electron charge and ζ an asymmetry parameter. In the case of ^2H nuclei ($I=1$) the ζ parameter for the C-D bond is very small, and equation (12) reduces to (13).^{66,67}

$$T_q^{-1} = \frac{3}{8} \left(\frac{e^2 q Q}{\hbar}\right)^2 \tau_q = \frac{3}{8} k_q^2 \tau_q \quad (13)$$

Here k_q is the deuterium quadrupole coupling constant, and depends on the nature of the C-D bond in the molecules studied.

The quadrupole relaxation time T_q is evaluated in a manner similar to that used for the evaluation of T_1 values from ^{13}C relaxation time measurements.⁴⁷

Measurements of quadrupole relaxation times were performed on a Varian XL-100 spectrometer operating at 15 MHz for ^2H . The 90° pulse length and the time between pulses were 30 μs and 1 s, respectively.

III.4 Librational effects

The use of relaxation times (^{13}C or ^2H) and rotational correlation times observed for organic molecules is well documented.^{68,69} In recent years it has been pointed out that cross correlation terms, due to torsional vibrations in molecules, must be used for full interpretation of relaxation data.^{66,68-71} These librational motions always affect all sorts of relaxation time measurements so as to give T_1 values that are too high, which in turn leads to calculated internal correlation times (τ_i), that are too short and rotational barriers that are too low.

The extent to which librations influence estimated T_1 values is hard to predict, since very few studies have dealt with this problem. But it can be stated that the lower the rotational barrier, the greater the effect of these cross correlation terms, especially if the initial state is a very shallow minimum on the potential curve. An attempt to estimate the extent of librational motions in molecules in solution has been made recently by Levy *et al.*⁶⁹. In connection with a study of the internal rotation in 3 and 4-aminobiphenyl systems and the corresponding ammonium ions, Levy *et al.*⁶⁹ made a semiquantitative evaluation of the effects due to torsional vibrations, from ^{13}C spin lattice relaxation data.

A more quantitative study of the librational effect has been made by Johnson⁷⁰, who calculated T_1 values on a theoretical basis for methyl protons in solids (in the absence of vibrational effects). Johnson then compared his theoretically calculated T_1 values with measured relaxation times in the literature^{71,72,73}, and found that measured relaxation times are 41 % higher in magnitude than those calculated on a theoretical basis by neglecting cross correlations.⁷¹ This will in turn make estimated barriers from relaxation time measurements 10-15 % less in magnitude than if librational effects are neglected.

IV. THE MOLECULAR MECHANICS CALCULATION METHOD

As mentioned in the introduction, the molecular mechanics method was applied to aromatic systems with alkyl, haloalkyl, vinyl and formyl substituents.

The molecular mechanics method is based on the early work of Hill^{74,75} and Westheimer^{76,77} in their studies of molecular conformational energies. Since the work of Hill and Westheimer in the 1940:s, the molecular mechanics method has been developed and refined, and today many programs exist for performing molecular mechanics calculations.^{78-92,94-99} In this work, two of them have been used^{93,100}, namely the molecular mechanics program of Mislow *et al.*⁹⁰⁻⁹² (BIGSTRN) from 1971 and that of Allinger *et al.*⁹⁴⁻⁹⁹ (MMP1) from 1973.

In all molecular mechanics programs the total steric energy of a molecular system (E_{Total}) is written as the sum of several energy contributions (14).^{78,80}

$$E_{\text{Total}} = \Sigma E_{\text{Stretch}} + \Sigma E_{\text{Bend}} + \Sigma E_{\text{Torsion}} + \Sigma E_{\text{Nonbonded}} + \\ + \Sigma E_{\text{Out-of-plane}} + \Sigma E_{\text{Stretch-bend}} + \Sigma E_{\text{Torsion-bend}} + \Sigma E_{\text{Dipole}} \quad (14)$$

The steric energy E_{Total} is then minimized by a more or less efficient minimization method.^{78-92,94-99} Each energy term in equation (14) is described by an appropriate potential function and the summations are taken over all interactions in the molecule.

The first four terms in equation (14) arise from stretching or compression, angle-bending, torsion and non-bonded interactions. The "out-of-plane" term refers to the energy due to deviations from the planarity of an sp^2 hybridized group of atoms, while the stretch-bend and torsion-bend terms refer to a coupling between stretching and bending and between torsional and bending degrees of freedom, respectively. The dipole term accounts for the contribution of dipole-dipole interactions.

The molecular mechanics program of Mislow *et al.*⁹⁰⁻⁹² (BIGSTRN), which uses the force field of Allinger *et al.* (1971),⁹⁴ neglects the last two terms in equation (14). As the BIGSTRN program neglects effects due to p- π conjugation, the program can not be applied to aromatic ring systems, which are conjugated with groups such as acyl, vinyl or formyl groups.

The molecular mechanics program of Allinger *et al.* (MMP1), which uses a force field developed by Allinger *et al.* between 1971-1973, contains all of the terms

in equation (14).^{95-99,101,102} The MMP1 program is also applicable to aromatic systems conjugated with groups such as acyl, vinyl and formyl groups.

It must be borne in mind on comparing measured results in the liquid or solid state to those calculated, that energies calculated with the two programs BIGSTRN and MMP1 refer to gas phase processes at 25 °C.^{91,95,96} MM calculations have none the less been of great value and are utilized very much because they are more rapid and give results at a lower cost than those from quantum mechanical calculations.⁹⁷ The MMP1 program of Allinger et al. which has a very efficient minimization routine, has been shown for some aromatic systems to perform calculations giving structures and energies that are about one order of magnitude more accurate than those obtained by the MINDO method, and the time required for the calculations is two or three orders of magnitude less.⁹⁷

V. THE 1,3,5-TRINEOPENTYLBENZENE SYSTEM

As mentioned in the introduction, MM calculations with the BIGSTRN program package on TNB:s provided support for an interpretation of experimental results (^1H or ^{13}C NMR) on 2,4,6- Br_3TNB , $-\text{Cl}_3\text{TNB}$ and $-(\text{CH}_3)_3\text{TNB}$ in terms of attractive steric effects among the t-butyl groups.^{18,19} When Allinger's MMP1 program became available, it was decided to take advantage of its very efficient minimization routine and its dihedral angle driver to undertake a more thorough exploration of the internal rotational barrier.

The calculations were compared with experimental estimates of the barrier in TNB by ^{13}C and ^2H relaxation time measurements.

V.1 ^{13}C relaxation time measurements

Carbon-13 NMR spin-lattice relaxation times (T_1) were measured for both the unsubstituted aromatic carbons (T_{1m}) and the benzylic carbons ($T_{1\alpha}$) in TNB (1; page 4). Measurements of the nuclear Overhauser effect showed that the relaxation of the benzylic and aromatic carbons is completely dominated by dipolar relaxation (chapter III.2).

In order to use the relaxation times to calculate the correlation time for the overall motion of the molecule and that for the internal rotation of the neopentyl groups, the following assumptions were made⁴⁶: 1) the molecule as a whole tumbles isotropically (i.e. it may be approximated as a sphere); and 2) the internal rotation can be described as a diffusion process, i.e. it can be thought to proceed via a large number of small steps. With these assumptions, the equation due to Woessner⁵³ can be used to calculate the correlation time for the internal rotation. The Woessner equation in the form given by Brevard, Kintzinger and Lehn⁵⁴ was used (equation 6, chapter III.1). In equation (6) N_α is two because each benzylic carbon has two protons.

The angle β (110.1°) in equation (6) and the carbon-proton distances r_α and r_m (1.0968 and 1.0910 Å for the benzylic and aromatic bonds, respectively) were obtained from MM calculations.

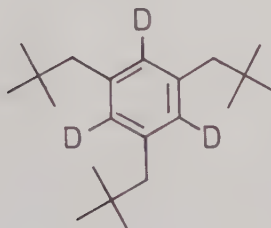
However, Stark et al.¹⁰³ have shown that the r_m value to be used for the bond length of the aromatic hydrogens should be 1.114 Å instead of the "normal" 1.09 Å, because effects of vibrational averaging must be taken into account.¹⁰³⁻¹⁰⁵ Since no "corrected" value for the bond length of the benzylic protons was given

by Stark *et al.*, the value of 1.1198 Å was used, which is the value for the aromatic hydrogen bond (1.114 Å) plus the bond length difference found from the MM calculations.

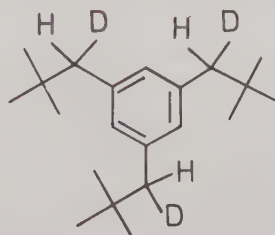
The free energy of activation at the temperature of measurement ($\Delta G^\ddagger$) was calculated via the Eyring equation (3) from the corresponding correlation time for the internal rotation (τ_i). The results are collected in Table 1.

V.2 ^2H relaxation time measurements

The deuterium spin-lattice relaxation times for aromatic and benzylic deuterons were measured on a solution containing equal amounts of compound (2) and the racemic compound (3).



(2)



(3)

From these relaxation times, the correlation time (τ_i) for the internal rotation could be calculated by the Woessner equation (6), as given by Brevard, Kintzinger and Lehn.⁵⁴ Assuming the deuterium quadrupole coupling constant (k_q) in eqn. (13) (chapter III.3) for both sp^3 and sp^2 type C-D bonds is 170 kHz,^{54,67} the value of $(3/8)k_q^2$ appropriate for the benzylic and aromatic deuterons is $0.43 \cdot 10^{12} \text{ s}^{-2}$. The calculated τ_i interval and the resulting free energies of activation are given in Table 1.

Another use of measured ^{13}C and ^2H relaxation times could be to estimate values for the quadrupole coupling constants (k_q).¹⁰⁶⁻¹⁰⁹ Jackman *et al.*¹⁰⁶ used this approach for phenyl acetylene- d_6 and benzene- d_6 and calculated the quadrupole coupling constants from equation (15), where T_1^{DD} and T_q are the measured ^{13}C and ^2H spin-lattice relaxation times, and $r_{\text{C-H}}$ is the carbon-

TABLE 1. ^{13}C and ^2H relaxation times^a, correlation times^a and calculated free energies of activation

Nucleus	T/ $^{\circ}\text{C}$	T_1/s	$T_{1\text{m}}/\text{s}$	$\tau/10^{-12}\text{s}$	$\tau_{\text{m}}/10^{-12}\text{s}$	$\tau_i/10^{-12}\text{s}$	$\Delta G^{\ddagger}/\text{kJmol}^{-1}$	Solvent	Spectrometer
^{13}C	28	$2.28 \pm 0.11^{\text{b,c}}$	$1.73 \pm 0.08^{\text{b,c}}$	24 ± 1	31 ± 1	200 - 380	19 ± 1	CD_3COCD_3	JEOL FX-60
^{13}C	28	$1.80 \pm 0.10^{\text{b,d}}$	$1.36 \pm 0.10^{\text{b,d}}$	31 ± 1	39 ± 2	230 - 570	19 ± 1	CDCl_3	JEOL FX-60
^{13}C	27	$1.82 \pm 0.08^{\text{b,e}}$	$1.45 \pm 0.07^{\text{b,e}}$	30 ± 1	37 ± 2	290 - 710	20 ± 1	CDCl_3	Varian XL-100
^2H	27	$0.0579 \pm 0.0018^{\text{b,e}}$	$0.0514 \pm 0.0010^{\text{b,e}}$	40 ± 1	46 ± 1	630 - 1530	22 ± 1	CHCl_3	Varian XL-100

^a T_1 , $T_{1\text{m}}$ refers to measured T_1 values for benzylic carbons (deuterons) and aromatic unsubstituted carbons (deuterons). τ , τ_{m} and τ_i are the correlation times for benzylic carbons (deuterons), for molecular motion and for internal rotation.

^b Errors are 3σ (see page 14).

In the case of ^2H the τ and τ_{m} values are calculated by using the quadrupole coupling constant equal to 170 kHz (see text).

All T_1 values from ^{13}C relaxation times are twice the measured relaxation times (due to two protons).

^c Mean value of three measurements. ^d Two measurements. ^e Single measurement.

$$(e^2Qq/h) = 49.3 \, r_{C-H}^{-3} \, (\tau_1^{DD}/\tau_q)^{\frac{1}{2}} \quad (15)$$

hydrogen bond length, in Ångströms. Using the mean values of the ^{13}C and ^2H relaxation times for TNB in CDCl_3 solution (see Table 1), the resulting benzylic and aromatic C-D quadrupole coupling constants are equal to 196 ± 7 and 186 ± 7 kHz, respectively.

V.3 Molecular mechanics calculations

Allinger's MM program MMP1 (1973 force field)⁹⁵⁻⁹⁹ was used to calculate conformational energies on the potential surface for the rotation of one of the neopentyl groups in the lowest energy rotamer of TNB, with rotation angle increments of 5° (see Figure 3 curve A, next page; the driving angle θ_{1278} is defined in Figure 2).

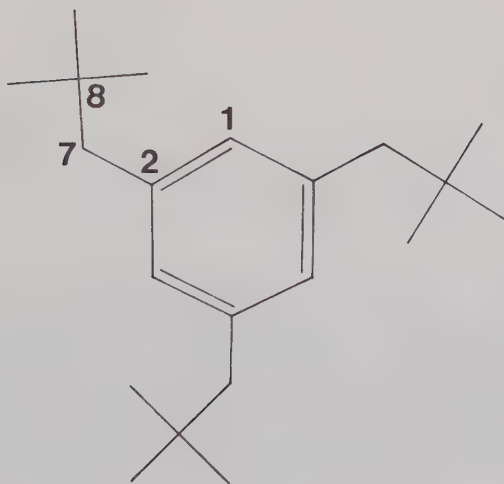


Fig. 2. Definition of the driving angle θ_{1278} in TNB.

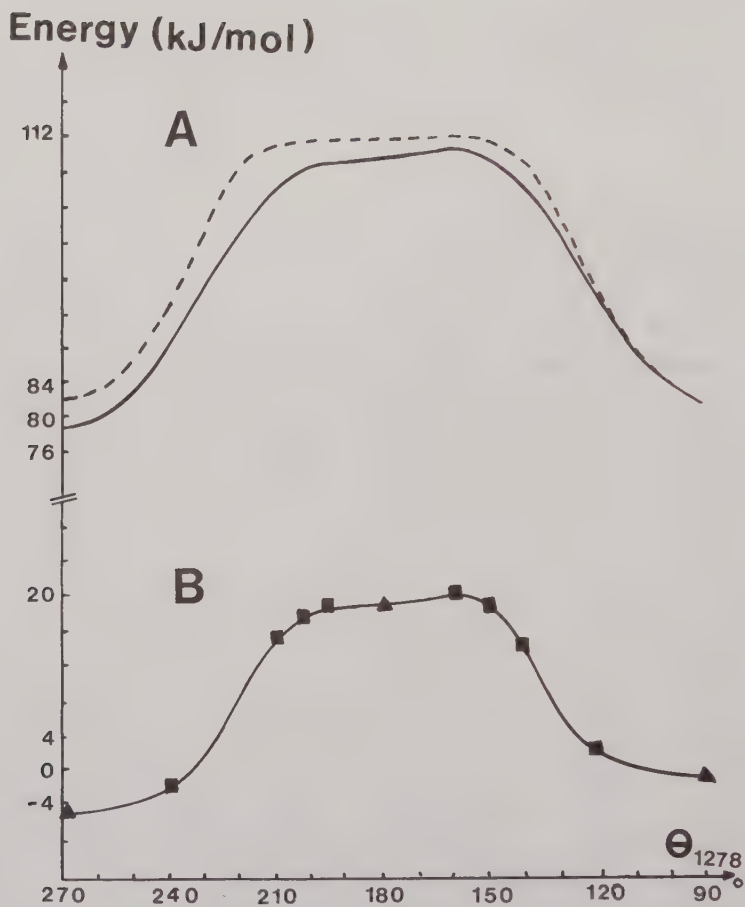


Fig. 3. Potential curves for the internal rotation of a neopentyl group in TNB, using the force field program MMP1 (curve A) and the BIGSTRN program (curve B), as a function of the driving angle Θ_{1278} . Values denoted $\blacktriangle$ are taken from Ref. 19. The dashed curve shows the energy profile for the rotamer "A = B = C" (page 5) by rotating one of the two neopentyls on the same side of the ring plane (see text).

In the calculations, all of the bond lengths and bond angles, as well as the torsional angles, except for that describing the rotation of the neopentyl group, were allowed to relax. For some selected torsional angles, the conformation obtained from the MMP1 program was used as the starting conformation for calcu-

lations with the BIGSTRN program. The energies resulting from these calculations are also shown in Figure 3 (curve B). The various energy contributions to the total energy for the two low energy conformations and for the transition state are collected in Table 2.

V.4 DISCUSSION

Molecular mechanics calculations

MM calculations by Carter and Stilbs¹⁹ on TNB were carried out with the BIGSTRN program package on a limited number of rotamers, viz that with all three *t*-butyl groups on the same side of the ring plane ("rotamer D", page 5) that with two on one side and one on the other ("rotamer A = B = C", page 5), and a rotamer with one neopentyl group twisted 90° from the starting conformation in "D". The energy profiles calculated with the BIGSTRN and MMP1 programs, are compared in Fig. 3. In the critical transition state region, the shapes of the energy profiles are quite similar, even though the total energies differ by 80-90 kJmol⁻¹ (Fig. 3). The difference in the total energies results from differences in the force fields used,^{90-92,94-99} as well as from the inclusion of an energy term resulting from a π -electron system calculation in the MMP1 program.⁹⁷ Both force fields indicate the operation of attractive steric interaction to be the dominant source of the energy difference between the two low energy conformations (cf. Table 2).

The asymmetry in the transition states in curves A and B shows the effect of attractive steric interactions. When one neopentyl group rotated so as to increase the distance between its *t*-butyl group and the other two, the steric attraction among the *t*-butyl groups should decrease. This decreased steric attraction is one of the factors (see Table 2) that causes the total conformational energy (E_{Total}) to be at a maximum (transition state) when the rotating group has its *t*-butyl group ca. 20° above the ring plane and the other two *t*-butyl groups below the plane. This geometry is shown in a stereo plot in Fig. 4. From this plot and also from the calculations, it is seen, as pointed out by Carter and Stilbs,¹⁹ that the "reaction coordinate" is primarily a combination of twisting about the $C_{\text{Ar}}-\text{CH}_2-$ and CH_2-C bonds.

A detailed inspection of the conformations at and close to the transition state given by the two programs shows that there are only minor differences. The largest difference is for the rotating neopentyl's methyl group closest to the ring, whose torsional angle (the angle $\text{CH}_3-\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-\text{CH}_2-\text{C}_{\text{Ar}}$) differs by 2-4°

TABLE 2. Calculated rotational barriers. Different energy contributions and total conformational energy (kJ/mol).

	Rotamer Θ_{1278}^a			Rotamer	Θ_{1278}^b		
	270	162	90		270 ^c	162	90 ^c
Compression	13.1	14.8	13.2	Bond-stretch	12.6	15.0	12.6
Bending	23.1	32.2	22.7	Angle-stretch	24.4	34.5	24.2
Stretch-bend	1.9	2.5	1.9	Torsion-stretch	0.8	3.7	0.8
Van der Waals (1.4)	46.9	49.7	46.7	Nonbond-stretch	-39.3	-28.7	-35.2
Van der Waals (other)	-27.5	-17.6	-23.7	Out of plane stretch	0.1	0.1	0.1
Torsion	20.9	28.3	20.8	Stretch-bend	-3.0	-4.5	-3.0
Torsion-bend	0.0	-0.9	0.0	Total	-4.4	20.2	-0.5
Dipole	0.5	0.5	0.5				
Total	78.9	109.6	81.9				

^a Calculated by the Allinger force field program MMP1 on the TNB system.

^b Calculated by the BIGSTRN program on the TNB system.

^c These calculations are taken from Ref. 19.

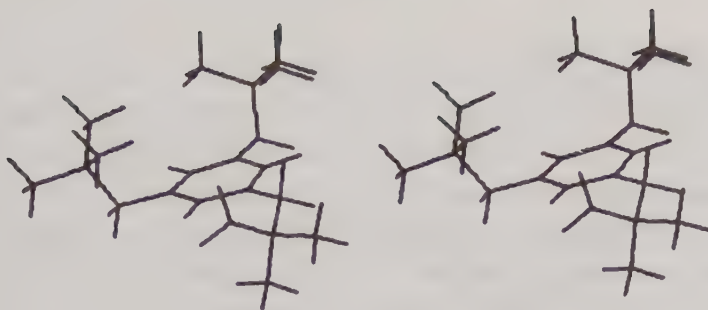


Fig. 4. Stereo plot of the transition state for internal rotation of a neopentyl group in TNB.

between the two programs in the vicinity of and at transition state.

Calculations were also made starting with the rotamer "A = B = C" and rotating one of the two neopentyls on the same side of the ring plane. The energy profile found is the dashed curve in Fig. 3A. From this energy profile (and from the calculations), it is seen that the energy of activation is ca. 30 kJmol^{-1} , and the energy profile is not symmetrical, although it may look so at first glance. As the two energy profiles in Fig. 3A show nearly the same free energies of activation (31 and 30 kJmol^{-1}), this implies that internal rotation along the dashed curve in Fig. 3A is as likely as rotation along the other curve for each of the rotamers "A = B = C".

The rotational barrier calculated with MMP1 (31 kJmol^{-1}) is slightly higher than that reported previously (24 kJmol^{-1} , see Table 2).¹⁹ Both calculated barriers are in reasonable agreement with the experimentally estimated upper limit of 23 kJmol^{-1} , based on an attempted NMR band shape study of a model compound (2-bromo-3,5-di-tert-butylneopentylbenzene). (The decoalescence of the $-\text{CH}_2-$ signal at low temperature could not be observed, only a broadening attributed to exchange).¹⁷ Since there are at least two routes by which a conformational change from one rotamer to another can take place, and in NMR band shape studies only the total process is observed, the observed value must

be corrected to take this into account before comparing with calculated barriers. However, if there are only two routes with the same activation energy, the correction is only $RT \ln 2$ (1.7 kJmol^{-1} at 300 K) on the free energy of activation.

^{13}C and ^2H relaxation times

A literature survey¹¹⁰ shows that there is an appreciable spread in the quadrupole coupling constants estimated by various methods. It is therefore difficult to know what value to use in this work, in order to use the ^2H relaxation times to estimate the correlation time for the internal rotation of the neopentyl groups. As shown in section V.2, the ^{13}C and ^2H relaxation times can be used to calculate the ^2H quadrupole coupling constant (k_q), resulting in values in good agreement with other quadrupole coupling constants obtained in the same way. However, an independent measurement of the quadrupole coupling constants is needed to be able to use relaxation times to estimate the effective correlation times for the deuterium nuclei. However, this does not exist, and a choice among various reasonable values¹¹⁰ had to be made.

As we shall see, the choice of quadrupole coupling constants can be critical for the calculated internal correlation time (τ_i). Assuming that both quadrupole coupling constants (k_q in eqn. 13) are 180 kHz, we get $\tau_i = 8.1 \cdot 10^{-10} \text{ s}$ by using values in Table 1 and eqn. (6). If we allow an uncertainty of $\pm 10 \text{ kHz}$ in the quadrupole coupling constants, and attempt to calculate the extreme limits for the internal correlation time (τ_i), we find at one extreme (benzylic: 170 kHz, aromatic: 190 kHz) that eqn. (6) is not satisfied, while at the other (benzylic: 190 kHz, aromatic: 170 kHz) a τ_i value of $2.6 \cdot 10^{-10} \text{ s}$ is obtained.

Fortunately, as seen from Table 1, the large intervals in the calculated τ_i values (due to errors in the estimated $T_{1\alpha}$ and T_{1m} values and quadrupole coupling constants used) will have little effect on the estimated free energies of activation. The values agree well with the previously discussed measurements.^{17,19}

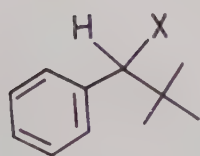
Conclusions

This work shows that the barriers to internal rotation calculated from ^2H relaxation time measurements are less reliable than those obtained from ^{13}C relaxation times, unless the quadrupole coupling constants for the molecular system studied are known from another independent measurement. Fortunately, as stated above, errors in the τ_i value (^2H relaxation times) will have very little effect on the calculated free energy of activation, but they should not be used in attempts to estimate activation enthalpies and entropies since they will most probably be seriously in error.

VI. SUBSTITUTED MONO-NEOPENTYLBENZENES

Reuvers *et al.*^{20,21} synthesised ring-substituted mono-neopentylbenzenes nearly ten years ago and studied the internal rotation around the $C_{sp^3}-C_{sp^2}^{(aryl)}$ bond by 1H NMR spectroscopy. The barrier to internal rotation could be estimated in only a few cases.

On the other hand, mono-neopentylbenzenes substituted in the benzylic position have rarely been studied by dynamic NMR methods. Exceptions are two papers by Baas *et al.*^{22,23}, who studied internal $C_{sp^3}-C_{sp^2}^{(aryl)}$ rotation in 4-alkyl-2-nitroacetanilides and in 1-hydroxy-1-alkyl-1-(3,4,5-trimethoxyphenyl)-2,2-dimethylpropanes (cf. compounds 14-19). It was therefore thought appropriate to more thoroughly study the hindered rotation in mono-neopentylbenzenes substituted in the benzylic position, and thus the following mono-neopentylbenzenes were synthesised, all of which were studied as racemates, except of course the achiral compounds (4) and (19).



(4) $X = H$

(5) $X = F$

(6) $X = Cl$

(7) $X = Br$

(8) $X = I$

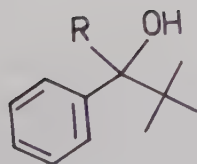
(9) $X = OCH_3$

(10) $X = OCOCH_3$

(11) $X = OSi(CH_3)_3$

(12) $X = CH_3$

(13) $X = CH_2CH_3$



(14) $R = H$

(15) $R = CH_3$

(16) $R = CH_2CH_3$

(17) $R = CH_2(CH_2)_2CH_3$

(18) $R = CH(CH_3)_2$

(19) $R = C(CH_3)_3$

TABLE 3. ^{13}C chemical shifts in neopentylbenzenes (in ppm) relative to TMS (at 28 $^{\circ}\text{C}$).

Substance	Substituted aromatic	Unsubstituted aromatic	Benzylic	Quaternary t-butyl	t-Butyl	Other	Solvent
4	137.1	130.0 (o) 127.0 (m) 124.8 (p)	48.3	30.1	27.3	-	CHCl_2F
5	134.6	127.4 (o+p) 126.8 (m)	104.7	33.7	23.1	$J_{\text{C-F}}=21.5\text{Hz}$	"
6	135.6	125.6 (o) 124.9 (m+p)	71.3	34.9	24.6	-	acetone-d ₆ / CS_2 (1:5)
7	136.1	124.6 (o) 123.3 (m) 123.0 (p)	66.3	34.9	25.2	-	"
8	137.7	125.2 (o) 123.5 (m) 123.2 (p)	50.4	34.9	26.1	-	"
9	144.6	128.3 (o) 128.0 (m) 127.7 (p)	92.1	35.6	26.2	37.3 OCH_3	"
10	136.3	125.1 (o+m+p)	79.5	32.3	23.1	172.5 C=O in CH_3CO 18.7 CH_3 in CH_3CO	CHCl_2F
11	140.7	125.5 (m) 124.9 (o) 124.2 (p)	79.6	33.5	23.1	-3.0 CH_3 in $\text{Si}(\text{CH}_3)_3$	"
12	145.3	129.1 (o) 127.9 (m) 126.1 (p)	49.9	33.6	27.8	17.9 CH_3	"

13	143.8	129.8 (o) 128.1 (m) 126.4 (p)	57.5	33.3	28.1	22.4 CH ₂ in CH ₃ CH ₂ ² CH ₃ in CH ₃ CH ₂ ² CH ₃ in CS ₂ (1:5) acetone-d ₆ /
14	141.8	128.3 (o) 127.8 (m) 127.3 (p)	81.8	34.6	26.2	- acetone-d ₆
15	143.7	127.4 (o) 126.5 (m) 125.7 (p)	77.1	37.6	25.4	24.1 CH ₃ in methyl "
16	142.0	128.1 (o) 126.9 (m) 125.9 (p)	80.2	38.3	25.6	26.5 CH ₂ in ethyl 8.3 CH ₃ in ethyl "
17	137.5	128.7 (o) 127.5 (m) 126.6 (p)	76.8	34.8	25.7	37.1 CH ₂ -O in butyl 26.4 CH ₂ -CH ₂ -O in butyl- 24.2 CH ₂ -(CH ₂) ₂ -O in butyl 14.0 CH ₃ in butyl "
18	146.7	127.2 (m) 126.4 (o) 125.5 (p)	80.8	38.6	27.7	34.1 CH in iso- propyl; 20.2 CH ₃ in isopropyl; 19.1 ³ CH ₃ in isopropyl DMSO-d ₆ / acetone-d ₆ (4:1)
19	146.8	129.0 (m) 128.8 (m) 128.3 (o) 127.0 (σ+p)	82.6	41.3	29.8	- DMSO-d ₆

VI.1 ^{13}C NMR measurements

For all compounds except compound (19), the ambient temperature (28°C) ^{13}C NMR spectra were of the type expected for rapidly rotating phenyl groups. For compound (19) the ^{13}C NMR spectrum was more complex than those for the other compounds, and consequently a slowly rotating phenyl group was assumed.

The t-butyl resonance in the ^{13}C NMR spectra of all compounds appeared as a single line, indicating fast rotation at 28°C . The ^{13}C NMR chemical shifts are summarized in Table 3.

The assignments of the unsubstituted aromatic carbons in Table 3 are based on the following assumptions: a) at fast neopentyl rotation the ortho carbons are more shielded (due to the substituent effect) and would then have a higher resonance frequency than the meta carbons^{49,51,52}; and b) at slow neopentyl rotation a greater difference in chemical shift may be found between the two nonequivalent ortho carbons than between the two nonequivalent meta carbons.⁴⁸

VI.2 Rotation around the $\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}^2}(\text{aryl})$ bond

For compounds (4), (5) and (14) the ^{13}C NMR spectra of the aromatic carbons remained essentially the same down to the lowest temperatures attainable (-142°C for 5 and -125°C for 14). For all other compounds more or less drastic changes occurred in the spectra as a function of temperature.

At temperatures where the neopentyl rotation is sufficiently slow, the aromatic carbons will reside in different chemical environments. One therefore expects the unsubstituted aromatic carbons to appear as five distinct peaks of equal intensities in the ^{13}C NMR spectrum. This is evidently what has been found for compounds (15), (16) and (17). (See Fig. 5). The peaks were in all cases assigned as the two non-equivalent ortho carbons to low field, the two nonequivalent meta carbons and the para carbon peak to high field.

In the case of compounds (7), (8), (9), (11) and (19) the same aromatic region showed only four resolvable peaks. For compounds (7) and (9), these patterns were assigned as an overlap between one of the nonequivalent meta carbons and the para carbon peaks. For compound (8), the four-peak pattern was the result of an overlap between the peaks due to one of the nonequivalent ortho carbons and one of the nonequivalent meta carbons. The latter case is exemplified in Fig. 6. In the case of compound (11) the four-peak pattern was the result of an overlap between the resonance from one of the nonequivalent ortho carbons and the para carbon.

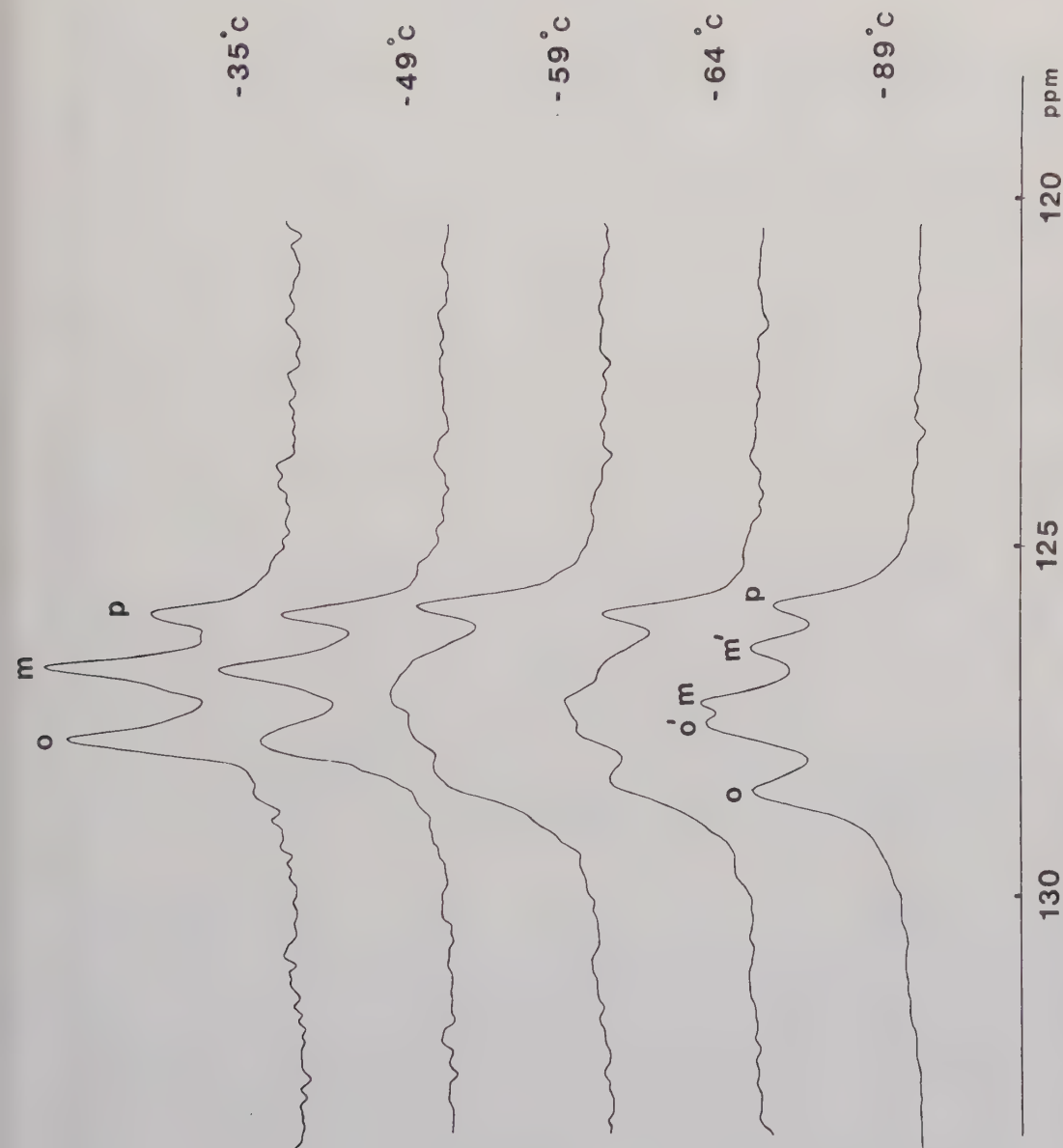


Fig. 5. Unsubstituted aromatic carbons in the ^{13}C NMR spectrum of compound (16) in acetone- d_6 solution at different temperatures.

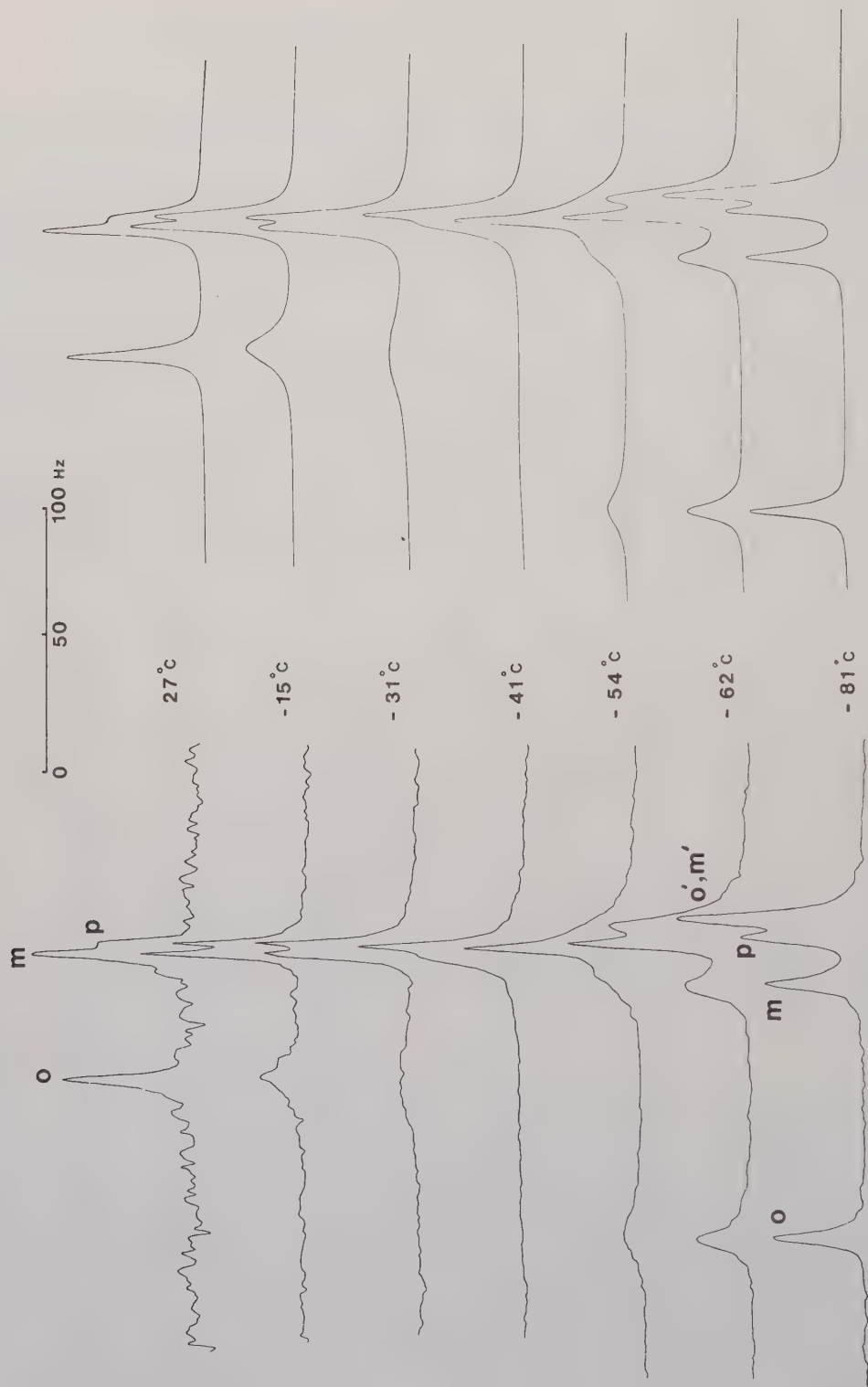


Fig. 6. Unsubstituted aromatic carbons in the ^{13}C NMR spectrum of compound (8) in $\text{CS}_2/\text{acetone-}d_6$ (5:1) solution at different temperatures (left) and iterated spectra (right).

For compound (19), as the temperature was increased the meta carbon resonances coalesced and the ortho carbon resonances broadened. At the highest temperature which could be reached (140 °C), due to apparatus limitations, the unsubstituted aromatic carbon region consisted of a sharp peak assigned to the meta carbons, a broad peak from the two ortho carbons beginning to overlap, and a third peak from the para carbon.

The unsubstituted aromatic carbons in the ^{13}C NMR spectra of compounds (6), (12) and (13) all showed three resolvable peaks at low temperature. For compound (13), the peaks were assigned as exemplified in Fig. 7: at low field one of the nonequivalent ortho carbons, the two unresolved meta carbons and an overlap between the other ortho and the para carbon peaks. In the case of compound (12), the o'-peak overlapped with the two meta carbon peaks, but in the case of compound (6), only the two nonequivalent ortho carbons were resolvable, and the two meta and the para carbon peaks overlapped to give a broad band.

The low temperature spectrum of compound (18) showed two peaks in the ratio 3:2, from the unsubstituted aromatic carbons (see Fig. 8). This pattern was assigned as an overlap between one of the two non-equivalent ortho carbons and the two unresolved meta carbons and an overlap between the other ortho and the para carbon peaks.

The unsubstituted aromatic region in the ^{13}C NMR spectrum of compound (10) at low temperature also consisted of two resolvable peaks (one broad) with intensity ratio 4:1. The small peak to high field was assigned to one of the nonequivalent ortho carbons, and the broad peak was assigned as an overlap of the signals from all the other unsubstituted aromatic carbons.

The low temperature chemical shifts for the unsubstituted aromatic carbons relative to the para carbon shift are collected in Table 4 for compounds (6)-(13) and (15)-(19).

Band shape analysis

The neopentyl group rotation is a two-site exchange between two identical sites (see Discussion). The temperature dependence of the aromatic ^{13}C NMR spectra has consequently been simulated as two-site exchanges. For compounds (6) and (10), only the resonances from the ortho carbons showed the expected temperature dependence, whereas for compounds (7)-(9), (11)-(13) and (15)-(19), both ortho and meta carbon showed the expected temperature dependence at sufficiently low temperatures. In the latter cases, the spectra were treated as two overlapping two-site cases with an extra Lorentzian signal, from the para carbon, unaffected by the exchange.

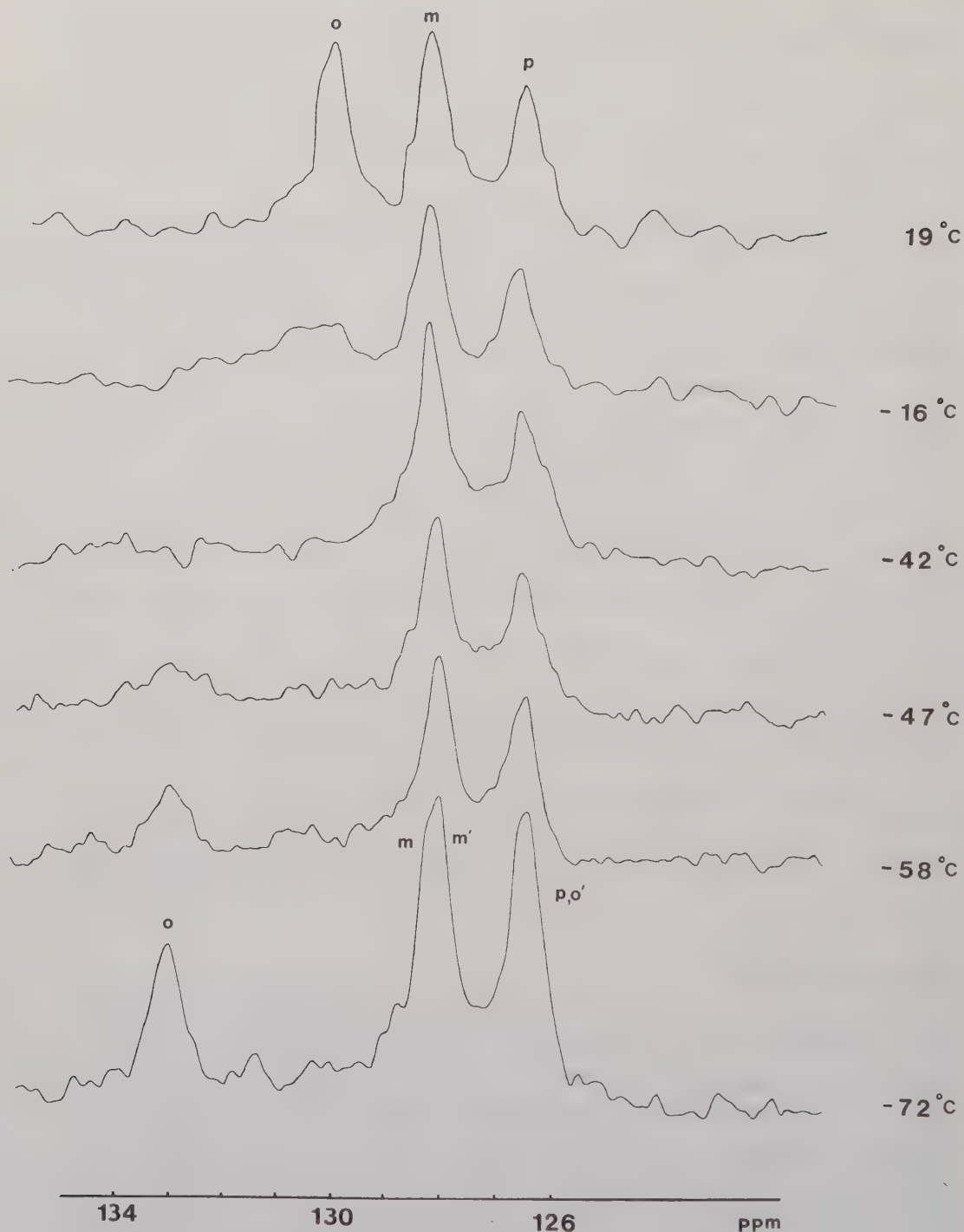


Fig. 7. Unsubstituted aromatic carbons in the ^{13}C NMR spectrum of compound (13) in $\text{CS}_2/\text{acetone-d}_6$ (5:1) solution at different temperatures.

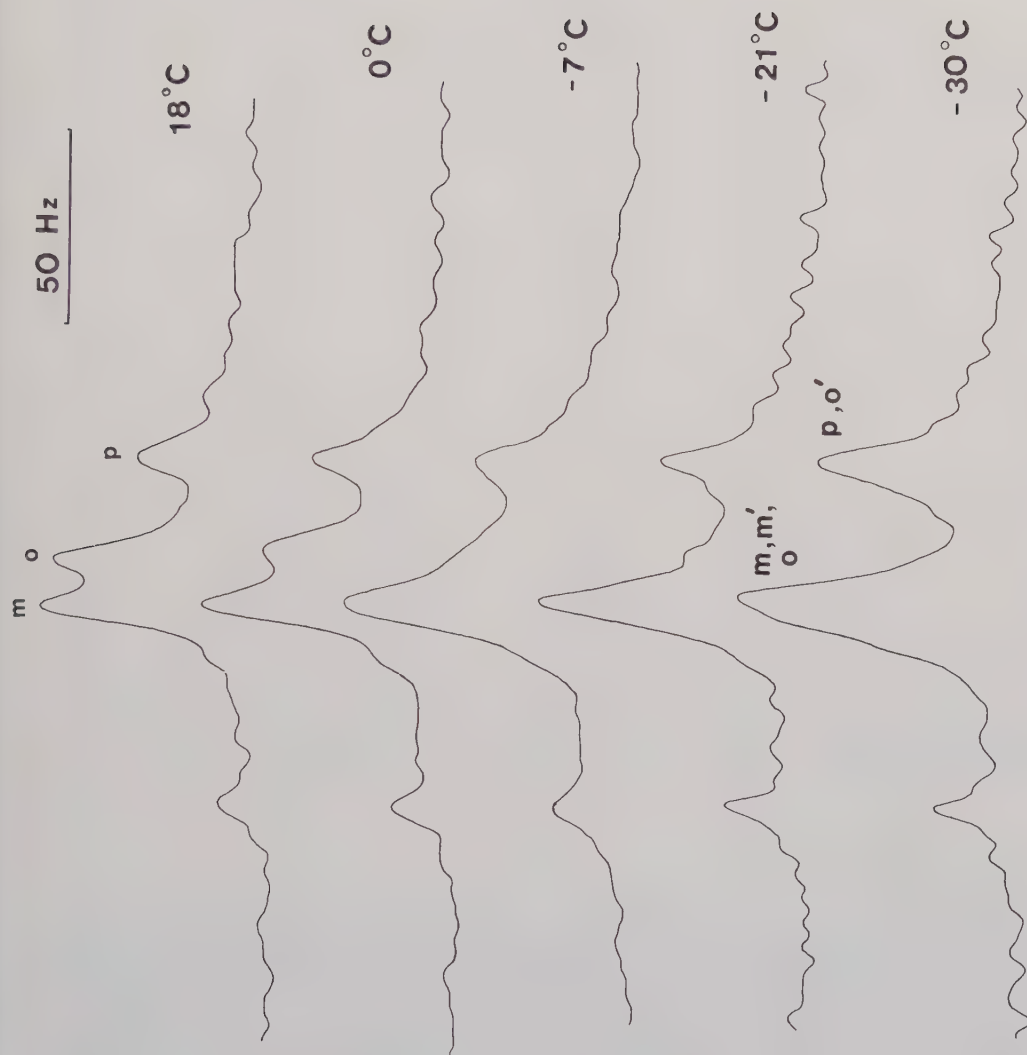


Fig. 8. Aromatic carbons in the ^{13}C NMR spectrum of compound (18) in $\text{DMSO-d}_6/\text{acetone-d}_6$ (4:1) solution at different temperatures. The small peak to the left is from the substituted aromatic carbon.

TABLE 4. Low temperature chemical shifts of unsubstituted aromatic carbons (ppm) relative to the para carbon shift in some mono-neopentylbenzenes.

Compound	Carbons			
	o	o'	m	m'
6	1.1	0.5	0	0
7	2.2	0.9	0.6	-0.1
8	5.0	-0.3	0.7	-0.3
9	1.5	-0.4	0.6	0
10	1.3	-1.2	0	0
11	1.5	-0.1	1.6	1.0
12	4.3	1.8	1.9	1.8
13	6.5	0	1.6	1.6
15	2.0	1.6	1.0	0.7
16	2.7	1.7	1.4	0.6
17	2.5	1.6	1.2	0.6
18	1.6	0.2	1.7	1.6
19	1.3	0	2.0	1.8

Note: Shifts to high field relative to the para carbon peak are given a negative sign.

For compounds (9), (12), (13) and (15)-(18) the para carbon signal was used as an internal resolution standard, whereas for compounds (6)-(8) and (19), the benzylic carbon resonance was utilized for this purpose.

The mean life times (τ) obtained from the band shape analysis were used to calculate the free energy of activation ($\Delta G^\ddagger$) by means of eqn. (3). The results are given in Table 5.

For a few compounds, the entropy ($\Delta S^\ddagger$) and the enthalpy ($\Delta H^\ddagger$) terms were also estimated, from the temperature dependence of $\Delta G^\ddagger$ (page 57).

TABLE 5. ^{13}C chemical shift differences ($\Delta\nu$, between ortho and meta carbons, respectively) and free energies to activation ($\Delta G^\ddagger$) for the neopentyl group rotation in some mono-neopentylbenzenes.

Compound	$\Delta\nu/\text{Hz}^a$	$\Delta G^\ddagger/\text{kJmol}^{-1}$	(T/ $^\circ\text{C}$) ^b	Solvent
6	16.0 ± 1.5^c	36.0 ± 0.9	(-95)	acetone- d_6 : CS_2 (1:5)
7	32.8 17.6 ± 1.5	40.9 ± 1.0	(-72)	"
8	134.0 26.0 ± 1.0	46.5 ± 0.7	(-41)	"
9	46.0 16.0 ± 1.0	40.2 ± 0.6	(-76)	"
10	63.0 ± 2.0^c	36.1 ± 1.6	(-93)	CHCl_2F
11	40.3 15.0 ± 1.2	35.0 ± 0.9	(-102)	"
12	64.0 3.0 ± 1.5	39.2 ± 0.5	(-75)	"
13	164.5 0 ± 1.0	46.2 ± 0.5	(-42)	acetone- d_6 : CS_2 (1:5)
15	9.0 8.0 ± 0.8	38.3 ± 0.5	(-89)	acetone- d_6
16	25.0 20.5 ± 1.0	46.1 ± 0.4	(-59)	"
17	22.0 15.5 ± 1.2	46.9 ± 0.7	(-53)	"
18	35.5 3.0 ± 1.0	52.2 ± 0.9	(0)	acetone- d_6 : $\text{DMSO}-\text{d}_6$ (1:4)
19	32.8 8.0 ± 1.0	90.5 ± 1.0	(138)	$\text{DMSO}-\text{d}_6$

^a Errors in chemical shifts ($\Delta\nu$) are estimated by changing $\Delta\nu$ until a difference between calculated and measured spectra can visually be detected.

^b Error in temperature $\pm 2^\circ\text{C}$.

^c Only the shift difference between ortho carbons could be estimated.

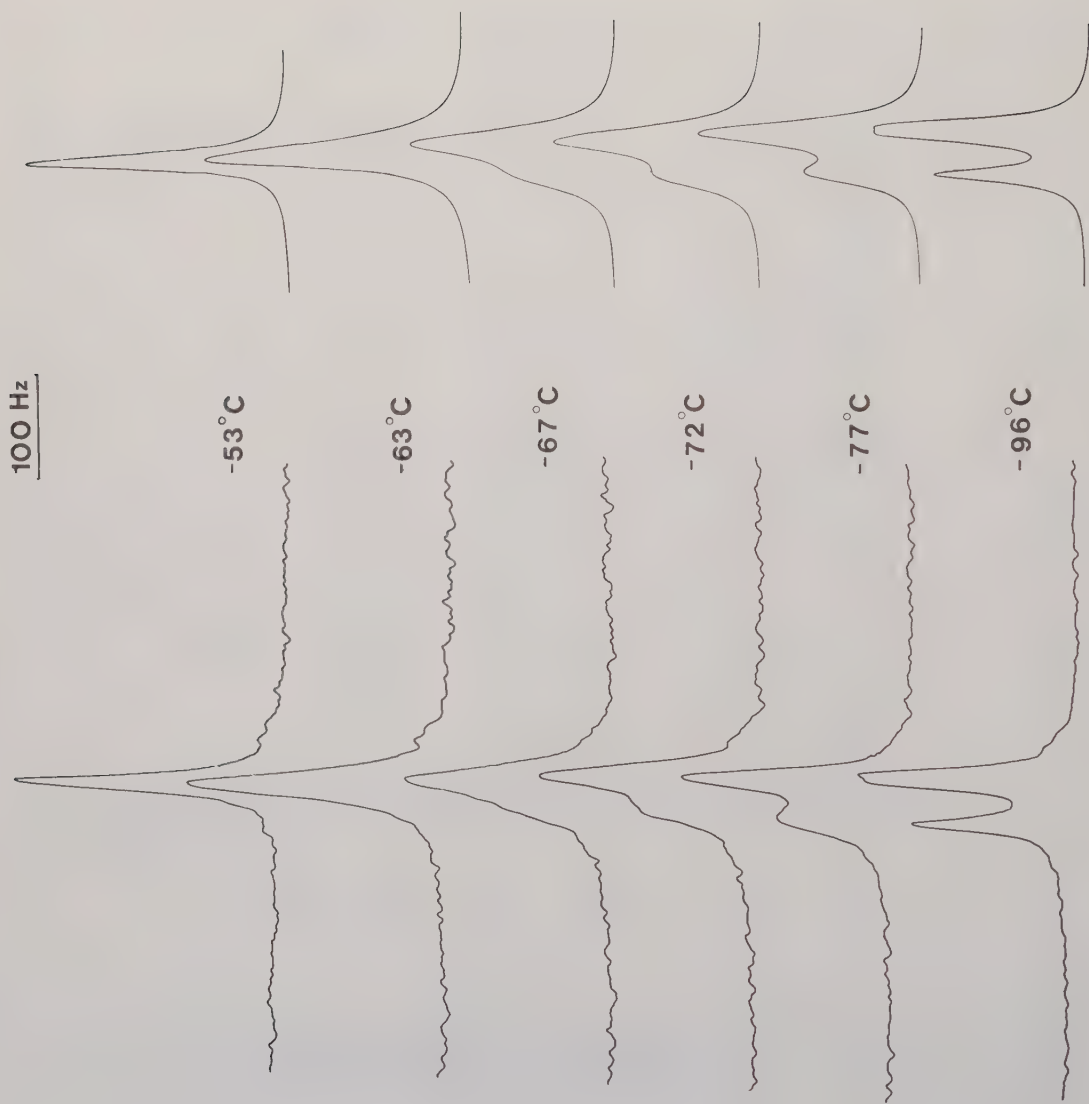


Fig. 9. Temperature dependence of the methyl resonances in the t-butyl group in the ^{13}C NMR spectrum of compound (19) in CHCl_3 solution (left) and calculated spectra (right).

TABLE 6. ^{13}C chemical shift differences ($\Delta\nu$) and free energies to activation ($\Delta G_T^\ddagger$) for the t-butyl rotation in some mono-neopentylbenzenes.

Compound	$\Delta\nu/\text{Hz}^a$	$\Delta G_T^\ddagger/\text{kJmol}^{-1}$	(T/ $^\circ\text{C}$) ^d	Solvent
5	150.0 ± 1.0	27.5 ± 1.0	(-118)	CHCl_2F
6	215.0 ± 1.0	32.4 ± 0.5	(-100)	"
7	39.2^b	34.9 ± 1.0	(-94)	acetone- d_6 : CS_2 (1:4)
8	50.1^b	35.5 ± 1.0	(-91)	"
9	187.9 ± 1.0	28.5 ± 0.4	(-105)	CHCl_2F
10	144.4 ± 1.0	27.5 ± 0.6	(-114)	"
11	198.7 ± 1.0	33.4 ± 0.5	(-104)	"
12	221.0 ± 2.0	26.4 ± 0.5	(-119)	"
13	205.0 ± 2.0	27.5 ± 0.4	(-112)	"
15	65.0 ± 1.5	31.8 ± 0.6	(-99)	"
16	18.8^b	33.0 ± 1.1	(-95)	"
17	$\begin{smallmatrix} 15.0 \\ 14.9 \end{smallmatrix} \pm 1.0$	36.0 ± 0.9^c	(-91)	"
18	$\begin{smallmatrix} 105.0 \\ 52.1 \end{smallmatrix} \pm 0.7$	37.1 ± 0.7^c	(-69)	"
19	$\begin{smallmatrix} 36.0 \\ 10.0 \end{smallmatrix} \pm 0.7$	41.1 ± 0.6^c	(-63)	"

^a Errors in chemical shifts ($\Delta\nu$) were estimated by changing $\Delta\nu$ until a clear difference between calculated and measured spectra could visually be detected.

^b Estimated shift differences from broadenings just below coalescence because low temperature spectra could not be obtained due to solubility problems or overlap from other signals.

^c Exchange among three uncoupled sites.

^d Error in temperature $\pm 2^\circ\text{C}$.

VI.3 Rotation around the $C_{sp^3}-C_{sp^3}$ bond

For all compounds except (4), one expects the t-butyl resonance (1H or ^{13}C) to split into three signals of equal intensities on slow t-butyl rotation, since the three methyl groups will then reside in different chemical environments. However, only for compounds (17)-(19) could three signals be resolved at a temperature low enough to slow down the t-butyl rotation sufficiently (Fig. 9). In all other compounds, there was apparently accidental chemical shift equivalence between two of the three ^{13}C methyl resonances, resulting in either a 1:2 or 2:1 doublet.

Band shape analysis

To estimate the t-butyl rotation rate for compounds (17)-(19), theoretical band shapes were calculated using a three-site exchange program. For all other compounds, the spectra were simulated as two-site exchanges with a 2:1 (or 1:2) population and the mean life time of the low population site was used to calculate $\Delta G^\ddagger$. (This simplified treatment is justified since every 120° twist of the t-butyl group will change the environment of the low population site, whereas only every second 120° twist will change the environment of the two carbons with the same shift).

For all compounds except (11), the quaternary t-butyl signal was used as resolution standard. For compound (11), the $Si(CH_3)_3$ signal was used for this purpose.

The free energy of activation ($\Delta G^\ddagger$) was calculated from the estimated mean life times for all compounds, and the results are summarized in Table 6. For compound (18), the entropy and enthalpy terms were also estimated, from the temperature of $\Delta G^\ddagger$ (page 60).

VI.4 Discussion

Neopentyl rotation. The calculated potential curve for the internal rotation of a neopentyl group in TNB (Fig. 3, chapter V) has a plateau-like shape, which has also been found from MM calculations on mono-neopentylbenzene (compound 4). (See Fig. 10, curve A). In the latter case, the potential curve (of height 26.7 kJ mol^{-1}), is of course completely symmetrical, in contrast to that of TNB. Curve A in Fig. 10 shows a rather steep increase in steric energy when the dihedral angle ϕ_{6178} (defined in Fig. 10) varies between 15° and 60° , since the t-butyl group and two of its methyls (denoted*) are forced to rotate, when the phenyl group rotates.

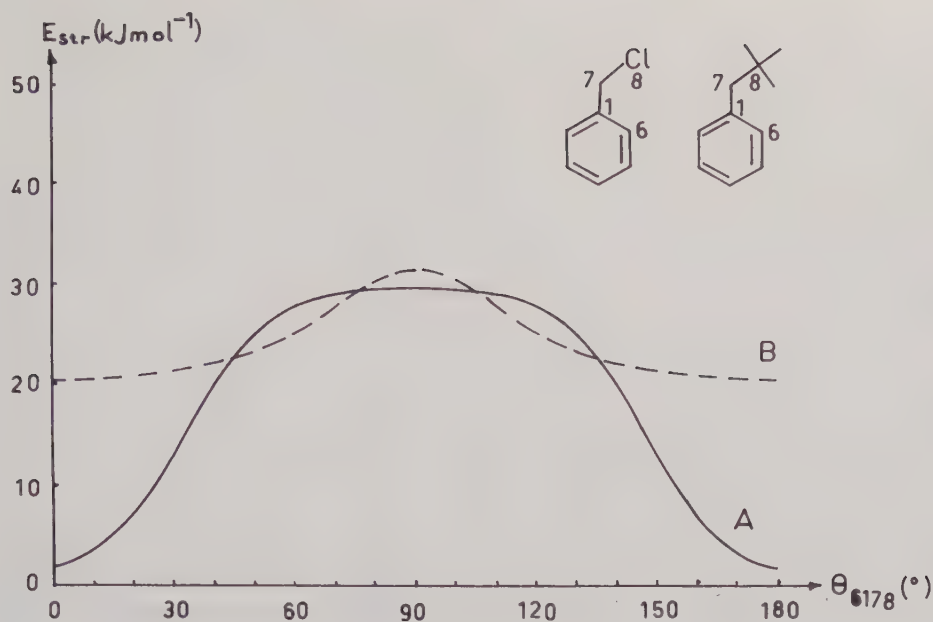
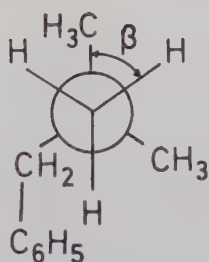
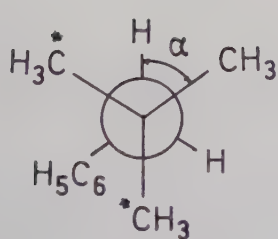


Fig. 10. Calculated potential curves for internal $C_{sp^3}-C_{sp^2}(\text{aryl})$ rotation in mono-neopentylbenzene (curve A) and benzyl chloride (curve B). The dihedral angle θ_{6178} is defined so that for values of 0° and 180° , the substituent is perpendicular to the ring plane.



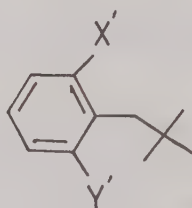
$\theta_{6178}/^\circ$	$\alpha/^\circ$	$\beta/^\circ$
0	60	58
20	62	50
40	67	38
60	72	16
80	66	13
90	60	15

When the angle θ_{6178} changes from 0° to 60° , the t-butyl group rotates 12° (α changes from 60° to 72°), both methyl groups rotate by 42° (β changes from 58° to 16°), and the steric energy increases drastically. When θ_{6178} changes from 60° to 90° , the t-butyl group rotates back into a staggered conformation ($\alpha = 60^\circ$), while the two methyl groups remain essentially in the same twisted positions (β varies only between 13° and 16°). The steric energy then remains essentially the same because the t-butyl group rotates back into a staggered conformation.

MM calculations on benzyl chloride lead to a more peaked potential curve, 10.7 kJmol^{-1} in height. (See curve B, Fig. 10). Curve B shows the greatest changes in steric energy when the dihedral angle θ_{6178} varies between 45° and 80° . In this case, the greatest nonbonded interactions between the chlorine and ring hydrogens are found when $\theta_{6178} = 90^\circ$.

For both curves (A and B), the initial state is calculated to be when the benzylic substituent (Cl or t-Bu) is perpendicular to the ring plane (conformer I, Fig. 11). In both cases, the transition state is found when the dihedral angle $\theta_{6178} = 90^\circ$ (conformer III, Fig. 11).

Reuvers *et al.*²¹ proposed conformer I (Fig. 11) to be the initial state for 2,6-disubstituted neopentylbenzenes (A). They also proposed the transition state



(A)

to be when $\theta_{6178} = 90^\circ$ and the t-butyl passes the smaller of the two ring substituents (X' and Y').

Compounds (4)-(13) all have two benzylic substituents (Table 5), and when the size of the smaller of the two substituents is varied (the largest is held constant), changes in neopentyl barriers are found. The neopentyl barrier changes from 36 to 41 to 47 kJmol^{-1} in mono-neopentylbenzenes (B) when the substituent (X) changes from Cl to Br to I (Table 5). The barrier for the fluorine-substituted compound was too low to be measured.

A similar trend was found for the methyl rotation in benzyl (C) and benzal halides (D) by Schaefer *et al.*^{45,111-127} from measurements of proton-proton

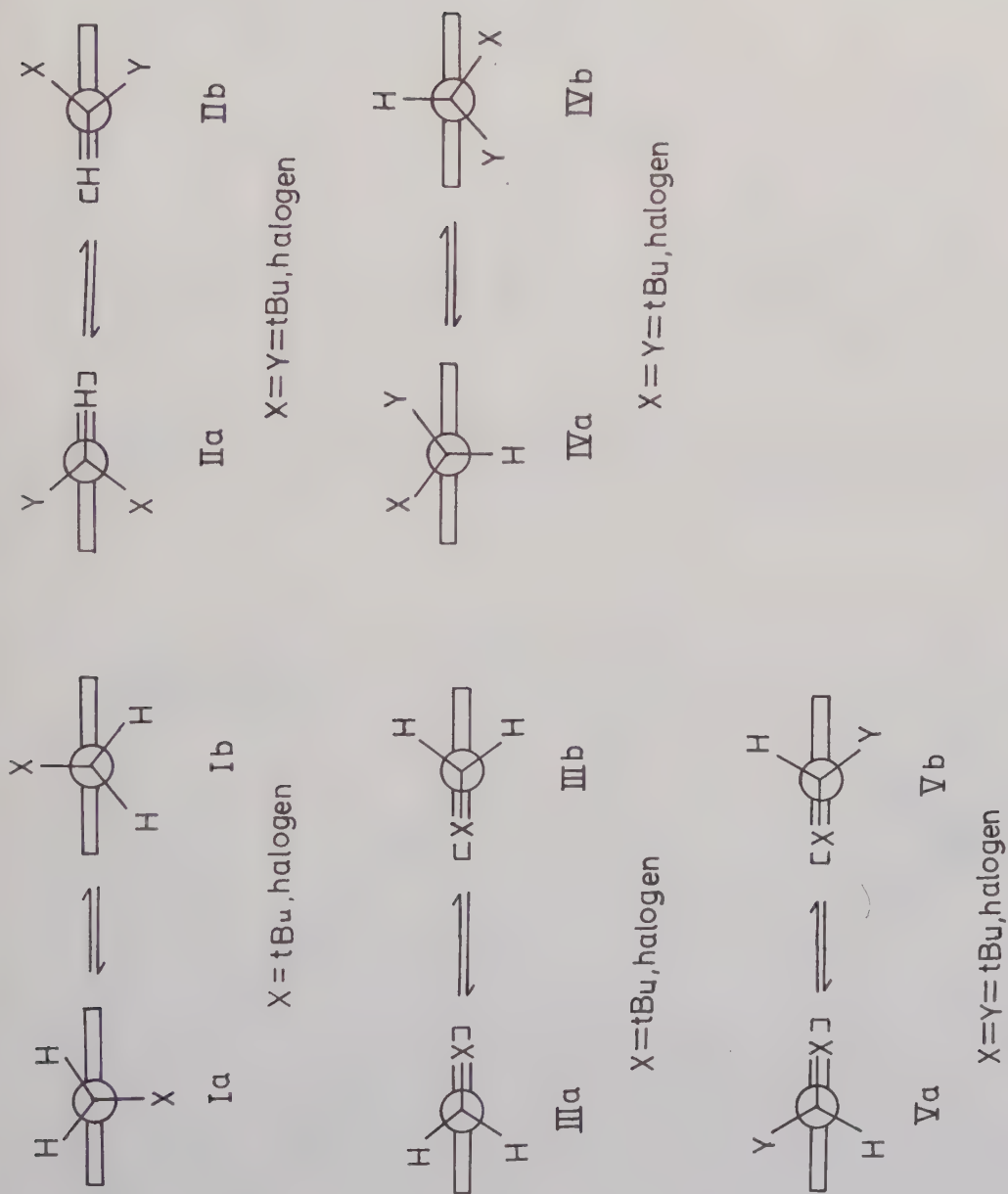
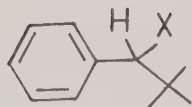
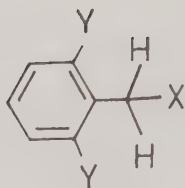


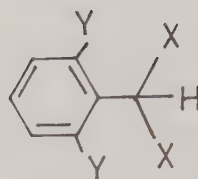
Fig. 11. Different conformers for rotation around a benzylic bond (see text).



(B)

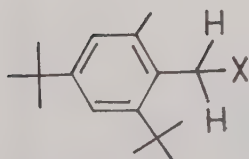


C1 Y=H
C2 Y=Cl

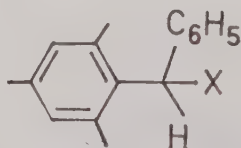


D1 Y=H
D2 Y=Cl

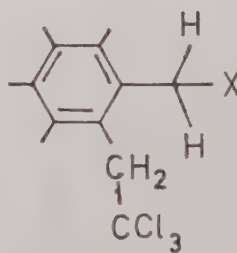
(proton-fluorine) long range coupling constants, and from DNMR measurements. Their results are given in Table 7 (next page), together with the results from measurements of torsional barriers in 2,4-di-*t*-butyl-6-methylbenzyl halides (E) by Cupas *et al.*,¹²⁷ and those of Mannschreck and Ernst^{128,129} from their studies on internal rotation in toluenes (F). The results from dynamic NMR studies of 2-trichloroethyl-3,4,5,6-tetramethylbenzyl halides (G) by Elzinga and Hogeveen are also presented.¹³⁰



(E)



(F)



(G)

When two benzylic substituents are present in the molecule, the potential curves in Fig. 10 may be used to give an indication of the nature of the initial and transition states. It is assumed that the effects from the potential curves in Fig. 10 are additive, which of course is a great oversimplification. For two identical large groups, e.g. two *t*-butyl groups, as benzylic substituents, the sum of two curves which are shifted 120° from each other will appear as shown in Fig. 12.

TABLE 7. Measured $C_{sp^3}-C_{sp^2}(\text{aryl})$ rotational barriers (kJmol^{-1}) for different molecular systems (see text).

Molecular system								
X	B	C1	C2	D1	D2	E	F	G
F	-	1.3	18.8	4.6	12.6	-	-	52.4
C1	36.0	8.4	36.4	8.4	62.8	47.3	47.3	54.9
Br	40.9	>13	44.8	14.7	77.0	52.3	53.2	56.9
I	46.5	>16	50.7	-	87.9	66.6	-	59.5

For the angle $\theta = 30^\circ$, there is a minimum on the total potential curve. This conformation, which is the initial state, corresponds to conformer II in Fig. 11, i.e. the benzylic hydrogen lies in the ring plane. The transition state conforma-

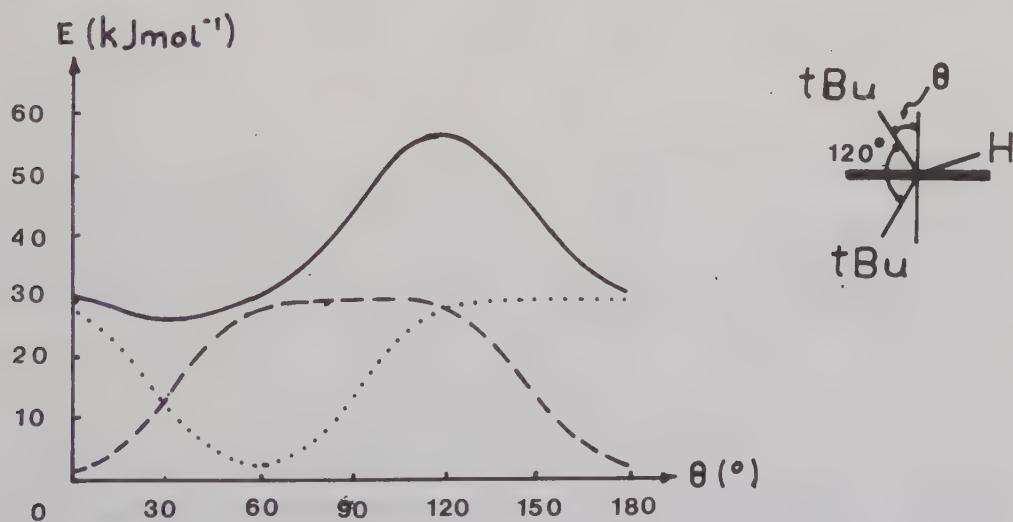
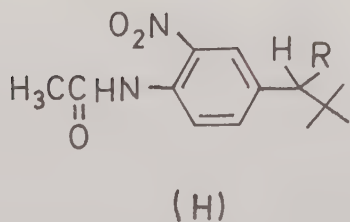


Fig. 12. Total potential curve (—) for $C_{sp^3}-C_{sp^2}(\text{aryl})$ rotation and potential curves (---,.....) for two benzylic t-butyl groups, separated by a 120° angle.

tion occurs when $\theta = 120^\circ$ (conformer IV in Fig. 12). The neopentyl barrier estimated according to Fig. 12 amounts to ca. 30 kJmol^{-1} . A comparison between Figs. 10 (curve A) and 12 indicates that the neopentyl barrier is only slightly increased when a benzylic hydrogen in mono-neopentylbenzene is replaced by a t-butyl group. These theoretical results are not in agreement with experiment. Baas²² studied compounds of type (H), and when $R = t\text{-Bu}$ a barrier to $C_{sp^3}-C_{sp^2}(\text{aryl})$



$R = \text{H, Me or } t\text{-Bu}$

rotation of 93 kJmol^{-1} was estimated, which is much greater than that indicated in Fig. 12. When $R = \text{H}$ Baas²² could not estimate the barrier, but in chapter V the neopentyl barrier in TNB was estimated to be $\sim 23 \text{ kJmol}^{-1}$. Thus the neopentyl barrier in mono-neopentylbenzene is probably $\leq 23 \text{ kJmol}^{-1}$. These experimental results show that the neopentyl barrier increases by ca. 70 kJmol^{-1} when a benzylic proton in mono-neopentylbenzene is replaced by a t-butyl group. An explanation for these discrepancies may be that for a compound with two benzylic t-butyls the $t\text{Bu}-C_{\alpha}-t\text{Bu}$ angle (where C_{α} is the benzylic carbon), shown in Fig. 12, is greater than 120° , due to steric interactions between the t-butyl groups. The transition state energy may then increase, as the t-butyls are forced nearer the ring plane. The initial state energy may then decrease, as the t-butyls are further from the ring plane in the initial state conformation, and the net result may then be a higher barrier to internal neopentyl rotation.

When two benzylic chlorines are present in the molecule, Fig. 13 indicates that the initial state occurs when $\theta = 30^\circ$ (conformer II in Fig. 11). The transition state occurs when $\theta = 90^\circ$ or 150° , and these conformations correspond to conformer V in Fig. 11 (i.e. one chlorine lies in the ring plane). Fig. 13 also indicates that the energy in this conformer is only 2.5 kJmol^{-1} greater than that in the conformer with $\theta = 120^\circ$ (conformer IV, Fig. 11; this is probably within the error of the approximation). The simple considerations in Figs. 12 and 13

indicate that even though both the di-chloro and di-*t*-butyl substituted compounds have the same initial state, they might not have the same transition states, due to the plateau-like shape of the curve for the neopentyl group.

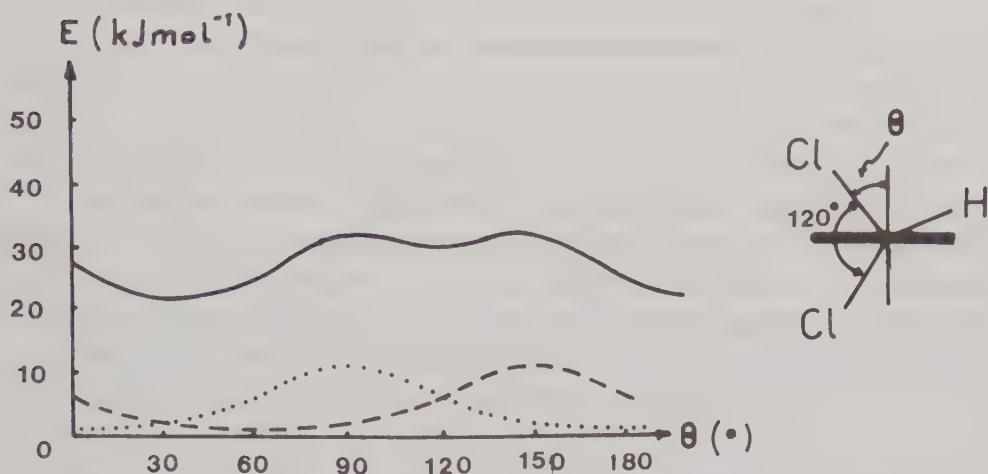
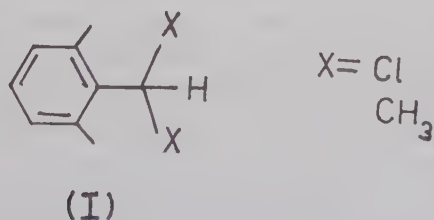


Fig. 13. Total potential curve (—) for $C_{sp^3}-C_{sp^2}(\text{aryl})$ rotation, and potential curves (---,....) for two benzylic chlorines, separated by a 120° angle.

In compounds of types D1 and D2, Schaefer *et al.*^{45,114-116,124-126} proposed initial and transition states to be conformers II and V (Fig. 11), respectively. Schaefer *et al.*^{45,115,116,119} also proposed conformer IV (Fig. 11) to have lower energy than conformer V. However, in compounds of type (I), Mannschreck



and Ernst¹²⁹ have found conformer IV to be the transition state conformation. They also point out that in performing such calculations, the entire molecule must be free to relax. This is of course of great importance, and is in contrast to the semiquantitative calculations of Schaefer *et al.*^{115,116,119}

Fig. 13 also indicates that the barrier in benzal chloride will be ca. 10 kJmol^{-1} , i.e. comparable to the barrier calculated for benzyl chloride itself (11 kJmol^{-1} , curve B in Fig. 10). In this case, the theoretical results are reasonable, and are in good agreement with experimental results of Schaefer *et al.*¹²², who found similar barriers for the molecular systems C1 and D1 when chlorine was the substituent (Table 7).

If the two benzylic substituents are different in size, i.e. one is a chlorine and one is a *t*-butyl group (as is the case for the systems studied here), Fig. 14 shows that the over-all shape is very much dominated by the larger group, as expected. The minimum on the potential curve occurs when $\theta = 10^\circ$, and this initial state differs by only 10° from that for the case of the unsubstituted neopentyl group (conformer I, Fig. 11). Even though the perturbation of the

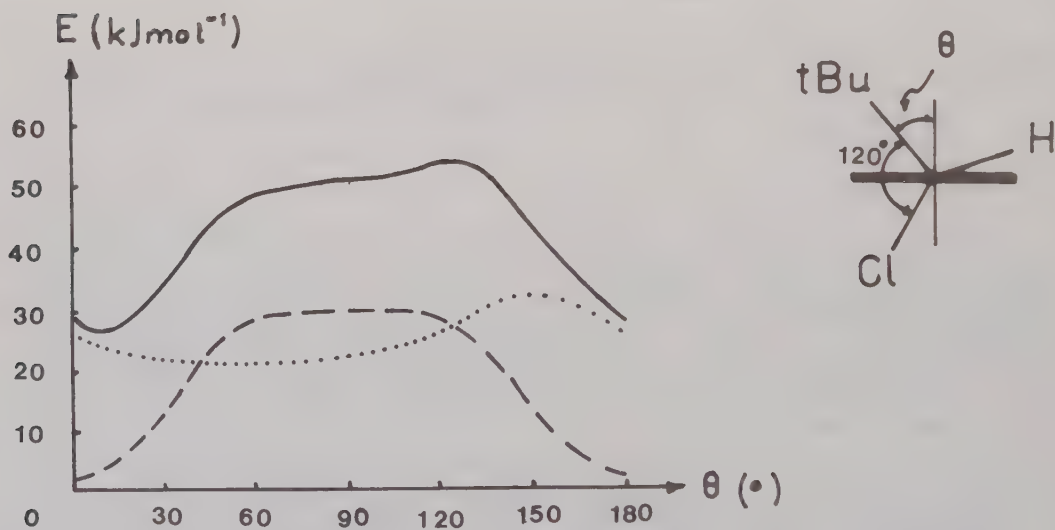


Fig. 14. Total potential curve (—) for $\text{C}_{\text{sp}}^3\text{-C}_{\text{sp}}^2(\text{aryl})$ rotation, and potential curves for a benzylic *t*-butyl group (---) and a benzylic chlorine (.....), separated by a 120° angle.

potential curve, due to the insertion of the chlorine, is quite small, the maximum has shifted from $\theta = 90^\circ$ to $\theta = 130^\circ$, and the transition state differs by only 10° from that in the case of two benzylic t-butyl groups (conformer IV, Fig. 11). The barrier to $C_{sp^3}-C_{sp^2}(\text{aryl})$ rotation indicated in Fig. 14 is 28 kJmol^{-1} , while the barrier experimentally estimated is 36.0 kJmol^{-1} (compound 6, Table 5). The larger barrier to rotation found experimentally may be explained as the result of the $\text{tBu}-C_\alpha-\text{Cl}$ angle in compound (6) being greater than 120° (as indicated in Fig. 14; cf. discussion of the compound in Fig. 12). Fig. 14 also indicates that the conformer corresponding to V (Fig. 11, $X = \text{t-Bu}$ and $Y = \text{Cl}$) has a slightly lower energy (4 kJmol^{-1} , probably within error due to additivity) than the indicated transition state.

Initial and transition state conformations indicated in Fig. 14 are in good agreement with results from MM calculations on the mono-neopentylbenzenes (12) and (13) with methyl and ethyl groups as benzylic substituents, respectively. According to the calculations, the initial state conformations are found when θ_{6178} (defined in Fig. 10) is 3° (12) and 8° (13), i.e. the initial state is mostly defined by the larger of the two substituents (cf. conformer I, Fig. 11, $X = \text{t-Bu}$ and one hydrogen replaced by Me or Et). The calculated transition states occur when θ_{6178} is 114° (12) and 120° (13) (cf. conformer IV). The calculated neopentyl barriers are 54.2 and 65.4 kJmol^{-1} for (12) and (13), respectively. (It was noted above in chapter V that the MMP1 program gives calculated neopentyl barriers that are too high). The experimentally estimated barriers are 39.2 (12) and 46.2 (13) kJmol^{-1} (Table 5). The MM calculations also show that conformations corresponding to conformer V in Fig. 11 are 15 (12) and 24 (13) kJmol^{-1} more stable than the corresponding transition states. A similar result is also indicated in Fig. 14 (compound 6). The $\text{tBu}-C_\alpha-\text{Me}$ and $\text{tBu}-C_\alpha-\text{Et}$ angles found from the calculations are 125° (12) and 127° (13) in the corresponding initial states, which give further support for the suggestion that the $\text{tBu}-C_\alpha-\text{Cl}$ angle in the compound in Fig. 14 in reality may be greater than 120° , in the initial state. In the transition states of compounds (12) and (13), however, the calculations show that the $\text{tBu}-C_\alpha-\text{Me}$ and $\text{tBu}-C_\alpha-\text{Et}$ angles are in both cases 120° , which is indicated in Fig. 14.

A comparison between Fig. 10 (curve A) and the approximate curve in Fig. 14 indicates that the neopentyl barrier will be the same whether or not a chlorine is introduced in the benzylic position in mono-neopentylbenzene. As mentioned above, the experimentally estimated neopentyl barrier in mono-neopentylbenzene is $\leq 23 \text{ kJmol}^{-1}$, and when one of the benzylic protons is replaced by a chlorine the experimentally estimated barrier is 36.0 kJmol^{-1} (compound 6, Tables 5 and 7). Experimental results thus show that there is an increase in neopentyl barrier of $\geq 13 \text{ kJmol}^{-1}$.

The theoretical results in Figs. 12 and 14 indicate that the neopentyl barrier is essentially unaffected when a benzylic chlorine is replaced by a t-butyl group. However, experimental results show that there is a large difference in neopentyl barrier. For the compounds in Figs. 12 and 14, the experimentally estimated neopentyl barriers are 93 and 36.0 kJmol⁻¹, respectively, i.e. a large effect on the neopentyl barrier is found when the effective size of the substituent changes. In addition to what has been pointed out above, it seems reasonable that the tBu-C_α-X angle increases as the effective size of the substituent X increases. In the discussions above (Figs. 12 and 14) it was proposed that a larger tBu-C_α-X angle will give a larger barrier to rotation, i.e. the molecule with two benzylic t-butyl groups should have the highest barrier.

When three benzylic substituents are present in the molecule, initial and transition states will probably be very similar to those discussed for the case where one of the substituents is much smaller than the other two. But when the smallest substituent increases in size so as to be comparable in size with either of the other two, the situation may change drastically.

The potential curves for three benzylic t-butyl groups have been added in

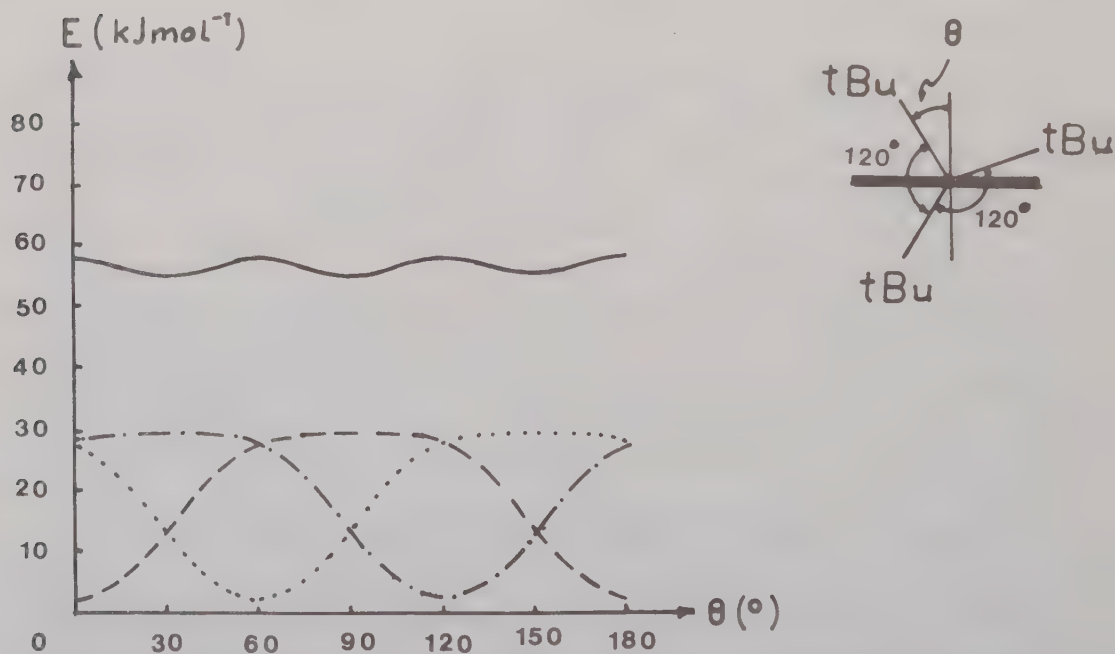


Fig. 15. Total potential curve (—) for C_{sp}³-C_{sp}²(aryl) rotation, and potential curves (---, ... and -.-) for three benzylic t-butyl groups, separated by 120° angles.

Fig. 15. The resulting curve shows minima when the angle θ has the values 30° , 90° and 150° . These initial state conformations correspond to conformer III (Fig. 11, if $X = t\text{-Bu}$ and the two benzylic hydrogens are replaced by $t\text{-butyl}$ groups). According to Fig. 15, the transition state occurs when the angle $\theta = 0^\circ$, 60° , 120° and 180° , which corresponds to conformer IV (Fig. 11, $X = Y = t\text{-Bu}$ and the benzylic hydrogen is replaced by a $t\text{-Bu}$ group). The rotational barrier is very small (3 kJmol^{-1}), because the initial states have high energy as a result of severe steric interactions among the $t\text{-butyl}$ groups. The transition state energy is here approximately the same as the case with two benzylic $t\text{-butyl}$ groups (cf. Fig. 12). However, no NMR measurements of the $C_{sp^3}\text{-}C_{sp^2}(\text{aryl})$ barrier in compounds with three identical benzylic substituents are available. This is expected, since the rotational barrier is probably too small to be estimated by dynamic NMR methods, and or the difference in chemical shift between the ortho carbons is almost certainly quite small.

Fig. 16 shows that if three chlorines are benzylic substituents, initial states are found when θ is 0° , 60° , 120° and 180° . Transition states are now

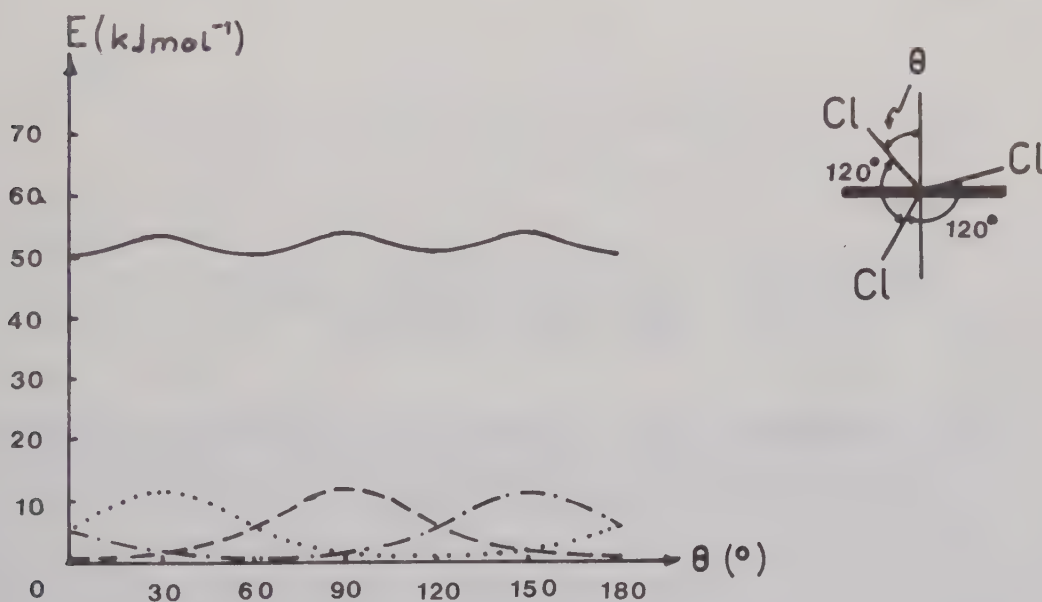


Fig. 16. Total potential curve (—) for $C_{sp^3}\text{-}C_{sp^2}(\text{aryl})$ rotation, and potential curves (---, ... and -.-) for three benzylic chlorines, separated by 120° angles.

found when θ is 30° , 90° and 150° . The difference between initial and transition states is also small in this case, 3 kJmol^{-1} . The initial and transition states change places if three benzylic t-butyl groups are replaced by three chlorines.

If two chlorines and one t-butyl group are benzylic substituents, the potential curve will be dominated by the shape of the curve for a neopentyl group (Fig. 17). Initial states occur for $\theta = 0^\circ$ and 180° , and transition states for $\theta = 55^\circ$ and 125° .

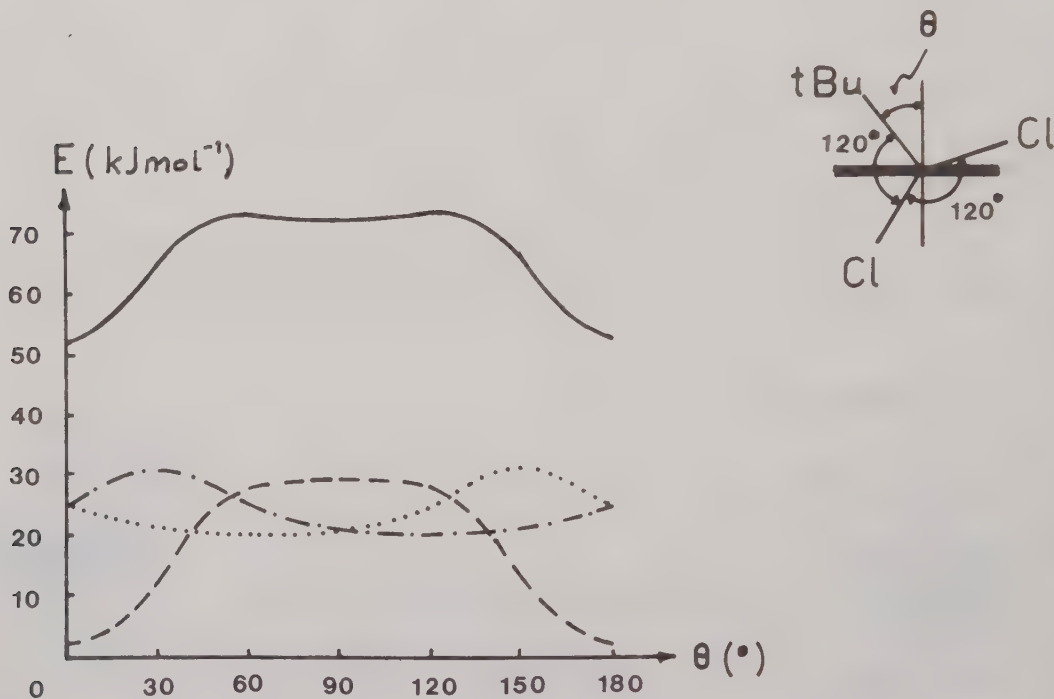


Fig. 17. Total potential curve (—) for $\text{C}_{\text{sp}^3}\text{-C}_{\text{sp}^2}(\text{aryl})$ rotation, and potential curves for a benzylic t-butyl group (--) and two benzylic chlorines (...,-.-), all separated by 120° angles.

When two t-butyl groups and one chlorine are the benzylic substituents, the potential curve is dominated by the shape of the curve for two t-butyl groups (Fig. 18). Initial states are found when $\theta = 5^\circ$ and 115° , and the transition state when $\theta = 60^\circ$.

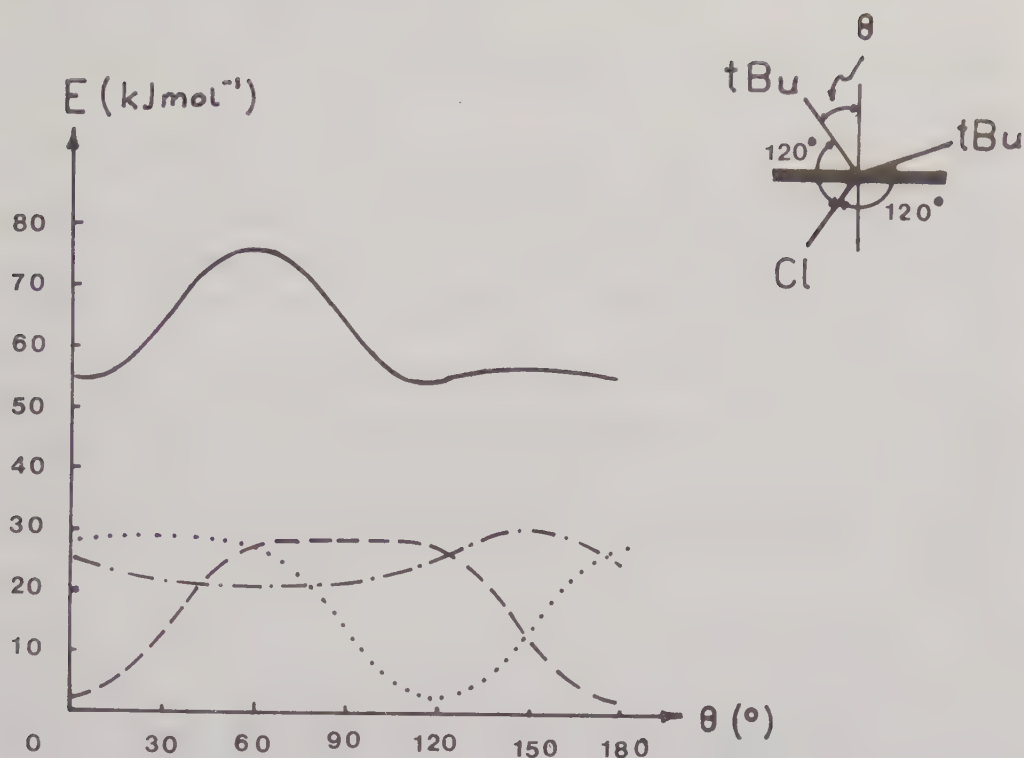


Fig. 18. Total potential curve (—) for $\text{C}_{\text{sp}^3}\text{-C}_{\text{sp}^2}(\text{aryl})$ rotation, and potential curves for two benzylic t-butyl groups (---,) and a benzylic chlorine (---), all separated by 120° angles.

Figs. 17 and 18 both indicate that the barrier to internal neopentyl rotation decreases when the benzylic hydrogen in compound (6) (Fig. 14) is replaced by a chlorine or a t-butyl group, since the initial states are raised more in energy than are the transition states. Anderson *et al.*¹³¹ found the neopentyl barrier in the para- (NO_2) -substituted compound (12) to decrease by 5 kJ mol^{-1} when the benzylic proton was replaced by a chlorine.

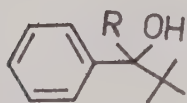
Comments on the results found for compounds (9)-(11)

When the substituents are acetate and trimethylsilyloxy groups (compounds 10 and 11), the measured neopentyl barriers ($\Delta G^\ddagger$) are 36.1 and 35.0 kJ mol^{-1} , respectively (Table 5), but when the substituent is a methoxy group (compound 9) the

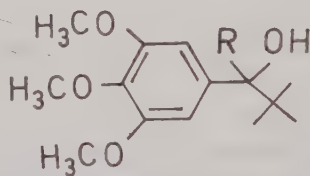
barrier is 40.2 kJmol^{-1} . These results may be explained because the carbonyl part of the acetate group is flat, and this part probably orients perpendicularly to the benzylic bond. The steric hindrance caused by the benzylic acetate group in compound (10) should then be less than that caused by the methoxy group in compound (9).

For silylethers, Si—O bond lengths of $1.633 \pm 0.005 \text{ \AA}$ are common in the literature^{132,133}, while those for O—CH₃ ethers are $1.435 \pm 0.005 \text{ \AA}$.¹³² The same relative bond lengths will probably exist for benzylic substitution, and thus the longer O—Si bond will make the Si(CH₃)₃ group in compound (11) be further from the benzylic position than the CH₃ group in compound (9), and thus alleviate the steric hindrance.

Compounds (14)-(19): A large effect on the $\Delta G^\ddagger$ -values for the C_{sp}³-C_{sp}²(aryl) rotation is observed in compounds of type (K), when one of the two benzylic substituents is varied (Table 5). The results are compared with those of Baas *et al.*²³ from ¹H NMR spectroscopic studies of the C_{sp}³-C_{sp}²(aryl) rotation in 1-hydroxy-1-alkyl-1-(3,4,5-trimethoxyphenyl)-2,2-dimethylpropanes (L), (see Table 8).



(K)



(L)

TABLE 8. Barriers to internal $C_{sp^3}-C_{sp^2}(\text{aryl})$ rotation (kJmol^{-1}) for some benzyl alcohols (see text).

Molecular system		
R	K	L
H	-	36.4 ± 1.2
Me	38.3 ± 0.5	39.4 ± 1.2
Et	46.1 ± 0.4	47.3 ± 1.2
n-Pr	-	47.3 ± 1.2
n-Bu	46.9 ± 0.7	47.7 ± 1.2
i-Pr	52.2 ± 0.9	54.4 ± 1.2
t-Bu	90.5 ± 1.0	$89.6 \pm 1.2^*$

* Gall et al.¹³⁴ estimated $\Delta G^\ddagger = 86\text{--}94 \text{ kJmol}^{-1}$ for this substance in DMSO-d_6 solution.

When the substituent $R = \text{H}$ in the K series, the barrier could not be estimated by ^{13}C NMR spectroscopy, probably due to shift equivalence. There is very good agreement between the estimated neopentyl barriers in series K and L (Table 8). It should however be noted that the measurements were not performed in the same solvent, except for the case $R = \text{t-Bu}$, where DMSO-d_6 was used as solvent in both cases.

When two t-butyls are benzylic substituents, Fig. 12 indicates conformer II (Fig. 11) to be the initial state. This conformation will probably remain as initial state when the benzylic proton is replaced by a hydroxyl group, since the t-butyls are much larger in size. This conformation, with the hydroxyl group in the ring plane, was also proposed by Baas et al.²³ and by Gall et al.¹³⁴, in their ^1H NMR spectroscopic studies, to be the initial state for the alcohol with two benzylic t-butyl groups. However, Bartlett et al.¹³⁵ reported two OH stretching bands due to free and π -bonded hydroxyl groups in compound (19) in CCl_4 solution, at room temperature. They suggested the form with free hydroxyl group to be conformer II, i.e. the OH should be in the ring plane, while the form with π -bonded OH groups should correspond to a conformation with the OH

group perpendicular to the ring plane. Gall *et al.*¹³⁴ gave another explanation, which is in better accord with the initial state conformation proposed above. One band should correspond to the conformation with the OH group in the ring plane, and the other band to a conformation in which the OH group is twisted a few degrees away from the aromatic ring plane and hydrogen bonded to the π -electron cloud above the edge of the ring.

Baas *et al.*²³ thought it to be very probable that the initial state conformation proposed for the di-*t*-butyl alcohol will also be the same when one of the two benzylic *t*-butyl groups is replaced by a *n*-Bu or an Et group. On the other hand, when one of the benzylic *t*-butyl groups is replaced by a H or a Me group, they thought the initial state to be different. As a possible initial state conformation in these cases, one in which the H or the Me group was in the ring plane was proposed. MM calculations on mono-neopentylbenzenes with Me and Et as benzylic substituents and without hydroxyls (compounds 12 and 13), have shown that initial and transition states are rather similar in both cases. (θ_{6178} defined in Fig. 10 differs by 3° between the initial states and by 6° between the transition states). This similarity will probably remain when benzylic hydroxyl groups are introduced in these compounds.

Gall *et al.*¹³⁴ suggested a transition state conformation for 3,4,5-trisubstituted phenyl-di-*t*-butyl carbinols when one of the two *t*-butyl groups passes the ring plane (conformer V, Fig. 11). This suggestion was based on inspection of models and no calculations were made. As pointed out at the beginning of this discussion (Fig. 12), such transition state conformation has lower energy than a conformation where $\theta = 120^\circ$ (conformer IV, Fig. 11), when the benzylic substituents are two *t*-butyl groups. Probably both the initial and transition states will be the same when the benzylic H is replaced by a OH group, because this group is much smaller than the two benzylic *t*-butyl groups. MM calculations, although on compounds where only one of the benzylic substituents is a *t*-butyl group (compounds 12 and 13), have shown that a conformer in which θ_{6178} (Fig. 10) is 90° has a lower energy than the transition state conformations. It is therefore more probable that conformer IV will correspond to the transition state conformation in the case of compound (19).

The barrier to internal neopentyl rotation found for compound (16) is (within the limits of error) the same as that for compound (17), (Table 5). The steric strain caused by the *n*-Bu group in compound (17) is thus probably the same as that due to the ethyl group in compound (16). A similar trend was also found by Baas *et al.*²³ in the L series.

Comparison of the neopentyl barriers found for the alcohols (15-19, Table 5) also shows that the difference in $\Delta G^\ddagger$ values between compounds (16) and (18)

is smaller than that between compounds (18) and (19). A moderate increase in neopentyl barrier of 6.1 kJmol^{-1} is found when one proton on the CH_2 carbon in the ethyl group in compound (16) is replaced by a methyl group. On the other hand, when the methine proton in the isopropyl group in compound (18) is replaced by a methyl group, an increase in neopentyl barrier amounting to 38.3 kJmol^{-1} is found. Baas *et al.*²³ also found a similar trend in the L series. They explained this difference as follows, which also may be applicable to the K series:

"Consider the strain present in the system $\text{R}-\text{C}_\alpha-\text{tBu}$ (C_α is the benzylic carbon) especially for $\text{R} = \text{tBu}$. In the initial state the groups R and t-Bu will be bent outwards. This outward bending will diminish the angle $\text{Ph}-\text{C}_\alpha-\text{tBu}$ and thus will increase the repulsive interactions in the transition state. Moreover, the steric strain in the transition state between the t-butyl group and the ortho carbon and hydrogen atoms of the benzene ring will diminish if the phenyl and t-butyl groups bend away from each other. The latter outward bending will be more difficult with the increase in the strain between the t-butyl group and the R group".

There is apparently a large difference in neopentyl barrier between compounds (9) and (14), the methoxy compound having a higher barrier (Tables 5 and 8). Mannschreck and Ernst¹²⁹ found a slightly lower barrier to internal $\text{C}_{\text{sp}}^3-\text{C}_{\text{sp}}^2(\text{aryl})$ rotation on changing from a hydroxy to a methoxy group in their substituted toluenes (F). They explain their results as the influence of hydrogen bonds operating in the alcoholic compound, because the ortho methyls had extreme shifts. In the neopentyl series K no ortho methyls are present in the aromatic ring, and the tendency to hydrogen bonding to the OH group should be much less in these compounds.

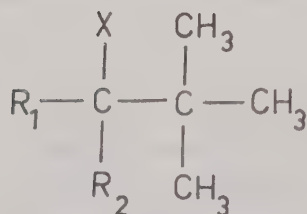
For a few compounds the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for internal neopentyl rotation were estimated (see Table 9).

TABLE 9. Activation parameters $\Delta H^\ddagger$ (kJmol^{-1}) and $\Delta S^\ddagger$ ($\text{Jmol}^{-1}\text{deg}^{-1}$) for the neopentyl rotation in some neopentylbenzenes.

Compound	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Solvent
7	40.2 ± 2.6	-7 ± 13	acetone- d_6 / CS_2 (1:5)
8	44.5 ± 1.9	-10 ± 8	"
12	37.6 ± 3.3	-8 ± 16	CHCl_2F
13	43.4 ± 2.0	-13 ± 9	acetone- d_6 / CS_2 (1:5)

The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values found for compounds (7), (8) and (12) are in good agreement with those estimated by Nilsson *et al.*¹⁷ for the neopentyl rotation in 2,4-dimethyl, 2,4-dibromo and 2,4-diiodoTNB. However, it must be borne in mind that the compounds were not measured in the same solvent, and in spite of the problems involved in estimating accurate entropies from NMR measurements, the $\Delta S^\ddagger$ term is known from work in the literature¹³⁶ to be sensitive to the medium.

C_{sp}³-C_{sp}³ rotation. For compounds (5)-(11) and (15)-(19) the steric hindrance to internal t-butyl rotation increases as the bulkiness of the benzylic substituent increases (cf. Table 6). t-Butyl rotations are not as frequently found in the literature as C_{sp}³-C_{sp}²(aryl) rotations, but papers have appeared by Hawkins *et al.*¹³⁷ and by Anderson and Pearson¹³⁸⁻¹⁴² on halogen-substituted ethanes (M)



M: X = halogen	R ₁ = Cl	R ₂ = H or alkyl
"	R ₁ = Br	"
N: "	R ₁ = CH ₃	"
O: "	R ₁ = H	R ₂ = CH ₃
P: "	R ₁ = R ₂ = H	
R: X = R ₁ = H or alkyl		R ₂ = alkyl
S: X = halogen or alkyl		R ₁ = C ₆ H ₅
		R ₂ = H

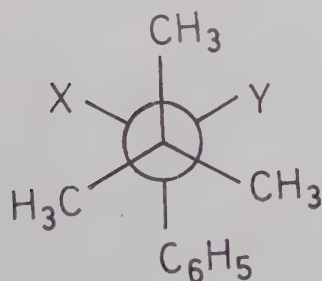
and (N). Freitag and Schneider¹⁴³ studied 2-substituted 3,3-dimethylbutanes (O) by ¹H NMR spectroscopy. They also made MM calculations with the Allinger MM1 program on substituted neopentanes (P). Bushweller and Anderson¹⁴⁴ have studied various alkyl substituted ethanes (R). The results of Hawkins *et al.*¹³⁷, Anderson and Pearson¹³⁸⁻¹⁴² and Freitag and Schneider¹⁴³ are compared with those from the mono-neopentylbenzene system (S) in Table 10.

TABLE 10. Barriers to internal t-butyl rotation ($\Delta G^\ddagger$ in kJmol^{-1}) for different molecular systems (see text).

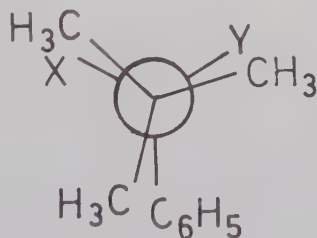
Molecular systems						
	M		N	O	P	S
	$(R_2 = \text{CH}_3)$		$(R_2 = \text{CH}_3)$			
X	$(R_1 = \text{Cl})$	$(R_1 = \text{Br})$	$(R_1 = \text{CH}_3)$			
H	-	-	29.2	20.5	15.1 ^a	-
F	-	-	33.7	-	-	27.5
Cl	45.3	49.8	43.7	32.2	21.3 ^a	32.4
Br	49.8	51.4	44.9	32.7	21.2 ^a	34.9
I	-	-	46.6	-	22.8 ^a	35.5
CH_3	41.1	45.2	-	28.1	16.1 ^a	26.4

^a Values from MM calculations with the Allinger MM1 program.

Table 10 shows excellent agreement in trends between the S series and the other series. Estimated t-butyl barriers for mono-neopentylbenzenes show a tendency to increase as the effective size of the halogen substituent increases. The staggered (S) and eclipsed (E) conformations are of course the initial and



S



E

X = substituent
Y = H or OH

transition states, respectively. These conformations have also been proposed by Anderson and Pearson¹⁴⁰⁻¹⁴⁴ and by Hawkins *et al.*¹⁷⁹

The t-butyl barriers estimated for the mono-neopentylbenzenes with benzylic methyl and ethyl groups (compounds 12 and 13 respectively), are the same within experimental error (see Table 6). Bushweller and Anderson¹⁴⁴ also observed that the t-butyl barrier in ethanes where the substituted carbon has one proton left (molecular system R) was nearly unchanged (within experimental error) as the bulkiness of the alkyl group substituent increased. This seems to indicate that¹⁴⁴ the initial state energy increases (due to steric interactions) as much as that of the transition state when the bulkiness of the substituent increases.

For compounds (15)-(19), where the benzylic carbon is quaternary, an increase in t-butyl barrier is found as the size of substituent increases.

Substituent	Me	Et	n-Bu	i-Pr	t-Bu
$\Delta G^\ddagger$ (kJmol ⁻¹)	31.8 $\pm$ 0.6	33.0 $\pm$ 1.1	36.0 $\pm$ 0.9	37.1 $\pm$ 0.7	41.1 $\pm$ 0.6

A similar trend in t-butyl barrier was found by Anderson and Pearson^{141,142} when X = Cl, R₁ = CH₃ and R₂ = alkyl group in the molecular structure N above. When R₂ varied from Me to Et and t-Bu the $\Delta G^\ddagger$ - value for internal t-butyl rotation was found to change from 44 to 45 and 49 kJmol⁻¹.

Only for compound (18) could the activation parameters be estimated. The enthalpy found is 39.6 $\pm$ 2.2 kJmol⁻¹ and the entropy 9 $\pm$ 11 Jmol⁻¹ deg⁻¹, i.e. the $\Delta S^\ddagger$ value can not be distinguished from zero.

Conclusions. Summations of calculated potential curves for toluenes with a chlorine or a t-butyl group as benzylic substituent have been used to predict initial and transition states for toluenes di- and tri-substituted in the benzylic position with Cl or t-Bu groups. The approximate summation, when the benzylic substituents are one Cl and one t-Bu group, indicates initial and transition state conformations, which are in good agreement with those found from MM calculations when the substituents are Me and t-Bu or Et and t-Bu. The approximate summations have thus proved useful to explain experimental results. Barriers to C_{sp}³-C_{sp}²(aryl) rotation indicated from the summations are found to be in agreement with experimental results when the benzylic substituents are chlorines, but discrepancies are found when t-butyl groups are substituents. In the case of two benzylic t-butyl groups the tBu-C_α-tBu angle (C_α is the benzylic

carbon) in reality probably deviates from 120^0 , which is assumed in the hypothetical summations.

Neopentyl barriers, estimated from ^{13}C measurements, are found to increase as the effective size of the benzylic substituent increases. Similarities between trends of results in the mono-neopentylbenzene systems and those of other systems are found.

Estimated t-butyl barriers in the mono-neopentylbenzene system show very good agreement with t-butyl barriers estimated in substituted ethanes.

VII. SUBSTITUTED 1,3,5-TRINEOPENTYLBENZENES

The TNB system with ring substituents has been very thoroughly investigated by Carter, Nilsson *et al.*^{8,12-18}, Carter and Stilbs¹⁹, Martinson⁷ and Dahlberg *et al.*⁹⁻¹¹, as pointed out in the introduction.

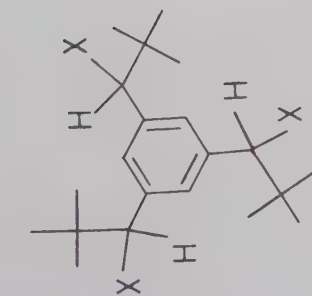
On the other hand, TNB systems with benzylic substituents have rarely been studied, except for two papers by Baas and Sinnema¹⁴⁵ and by Martinson.⁵ Martinson used ¹H NMR spectroscopy to examine the spectrum of the TNB compound 33 (next page) between -60 and 60 °C, and those of TNB:s substituted with hydrogens and hydroxyl groups and with hydroxyl and methyl groups in the benzylic positions (1,3,5-tris[1-hydroxy-2,2-dimethylpropyl]benzene and 1,3,5-tris[1-hydroxy-1,2,2-trimethylpropyl]benzene, respectively) at 40 °C. The spectrum of the latter compound was also examined at high temperatures (> 200 °C). For the two hydroxyl-substituted TNB:s Baas and Sinnema¹⁴⁵ made a complementary ¹H NMR study, and discussed the low temperature spectrum 1,3,5-tris(1-hydroxy-1,2,2-trimethylpropyl)benzene, but the barriers to internal rotation could not be estimated. It was therefore of great interest to apply dynamic NMR spectroscopy to TNB systems with benzylic substituents. The following TNB systems were synthesised, and were all studied as racemates expect, of course, the achiral compounds (28), (29), (31) and (33).

VII.1 ¹³C NMR measurements

The ¹³C NMR spectra of compounds (20)-(33) at ambient temperature (28 °C) all showed evidence for rapidly rotating neopentyl and t-butyl groups. The ¹³C chemical shifts are summarized in Table 11.

VII.2 Rotation around the C_{sp}³-C_{sp}²(aryl) bond

For compounds (20)-(27), (30) and (32), with three chiral benzylic centers, two diastereomeric pairs are possible, the RRR-SSS pair, and the RRS-SSR pair, using the Cahn-Ingold-Prelog R, S-nomenclature system.¹⁴⁶ In the case of the RRR or SSS isomer, both the unsubstituted and the substituted aromatic carbons will appear as singlets if the neopentyl groups are rotating rapidly on the NMR time scale. For the RRS or SSR isomer, these carbons may appear as doublets in



(20) $X = F$

(21) $X = Cl$

(22) $X = Br$

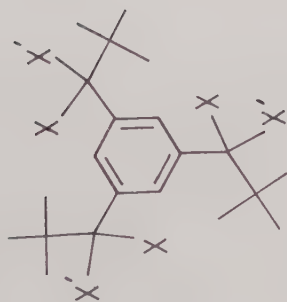
(23) $X = I$

(24) $X = OCH_3$

(25) $X = OCOCH_3$

(26) $X = OSi(CH_3)_3$

(27) $X = CH_3$



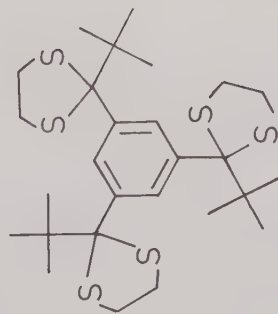
(28) $X = X' = F$

(29) $X = Cl \quad X' = Cl$

(30) $X = Cl \quad X' = CH_3$

(31) $X = X' = Br$

(32) $X = Br \quad X' = CH_3$



(33)

TABLE 11. ^{13}C chemical shifts in benzylic substituted 1,3,5-triisopentylbenzenes (in ppm) relative to TMS (at 25 $^{\circ}\text{C}$).

Compound	Substituted aromatic	Unsubstituted aromatic	Benzylic	Quaternary t-butyl	t-Butyl	Other	Solvent
20	128.1	126.7	102.3	34.4	23.8	-	CHCl_2F
21	133.7	124.6	71.1	35.3 ^a	25.2	-	acetone- d_6/CS_2 (1:5)
22	135.3	125.2	65.9	35.1 ^a	25.8	-	"
23	136.4	125.4	49.0	34.9 ^a	26.3	-	"
24	136.5	125.8 125.0	90.8	34.1	24.5	55.3 CH_3 in OCH_3^a	CHCl_2F
25	134.1	123.4 122.6	79.2	32.3	22.6	167.9 C=O in CH_3CO 18.6 CH_3 in CH_3CO^a	"
26	138.1	122.3	80.0	33.5	23.1	-3.0 CH_3 in $\text{Si}(\text{CH}_3)_3^a$	"
27	138.3	123.0	48.1	32.2	26.7	14.7 CH_3 in methyl ^a	acetone- d_6/CS_2 (1:5)
28	128.4	121.0	118.5	32.6 ^a	17.7	-	CDCl_3
29	132.0	124.1	96.9	39.4 ^a	20.0	-	"
30	132.5	121.5 120.5	77.7	37.6	24.6	25.2 CH_3 in methyl ^a	acetone- d_6/CS_2 (1:5)

31	132.2	126.9	83.9	40.3 ^a	21.0	-	CDCl ₃
32	136.6 136.2	129.2 125.9 124.4	79.6	39.1	26.3	27.7 CH ₃ in methyl ^a	acetone-d ₆ / CS ₂ (1:5)
33	139.5	129.8	84.8	39.1 ^a	27.5	37.3 CH ₂ in SCH ₂ CH ₂ S	"

^a Peaks used as internal resolution standards in band shape analyses.

a 1:2 (or 2:1) ratio. Thus, 6 possible signals may arise from the aromatic carbons in the ^{13}C NMR spectra of compounds (20)-(27), (30) and (32). Unfortunately, due to very small shift differences, fewer resolvable signals have been found in all cases. At temperatures where the neopentyl rotation is slow, the aromatic region in the spectra of these chiral compounds will be very complicated, and this pattern is analyzed in detail in the discussion.

The aromatic region in the spectrum of compound (20) remained essentially the same down to the lowest temperature attainable (-120°C).

At temperatures where neopentyl rotation is sufficiently slow, the unsubstituted aromatic carbon region in the ^{13}C spectra of the halogen substituted compounds (21)-(23) show clear substituent effects. When the benzylic substituents are iodine (compound 23), very large shift differences are found, and four signals are resolvable (Fig. 19). If bromines are the substituents (compound 22), the shift differences found are less and three peaks are resolvable, and when chlorines are the substituents (compound 21) the shift differences are so small that only one peak is observed. In the latter case, also at sufficiently slow neopentyl rotation, the substituted aromatic carbons showed three signals which could be used for band shape analysis.

At temperatures where the neopentyl rotation is sufficiently slow, the unsubstituted aromatic carbon region in the spectra of the oxygen-containing compounds (24)-(26) all show similar three-peak patterns. The chemical shift differences observed in all cases are somewhat greater than those observed when bromines are the benzylic substituents.

When the benzylic substituents are methyl groups (i.e. 27), very large chemical shift differences are observed for the unsubstituted aromatic carbons, at slow neopentyl rotation (Fig. 20). The chemical shift differences in this case are of the same magnitude as those observed when iodines are benzylic substituents. The shift differences observed for compound (27) are remarkable, since in the mono-neopentylbenzene series (Table 5, chapter VI) the methyl-substituted compound exhibits a chemical shift difference between the ortho carbons which is only ca. half of that found for the iodo-substituted compound. The reason for the large differences observed for compound (27) is not yet clear.

Three signals from the unsubstituted aromatic carbons are observed at ambient temperature for the bromo-substituted compound (32; Fig. 21). For the chloro-substituted compound (30), the chemical shift differences are smaller, and only two signals are observed. At slow neopentyl rotation the two partly overlapping signals in Fig. 21 (at 125.9 and 124.4 ppm, compound 32) are split into three signals of similar magnitude, as observed in the case of compound (30).

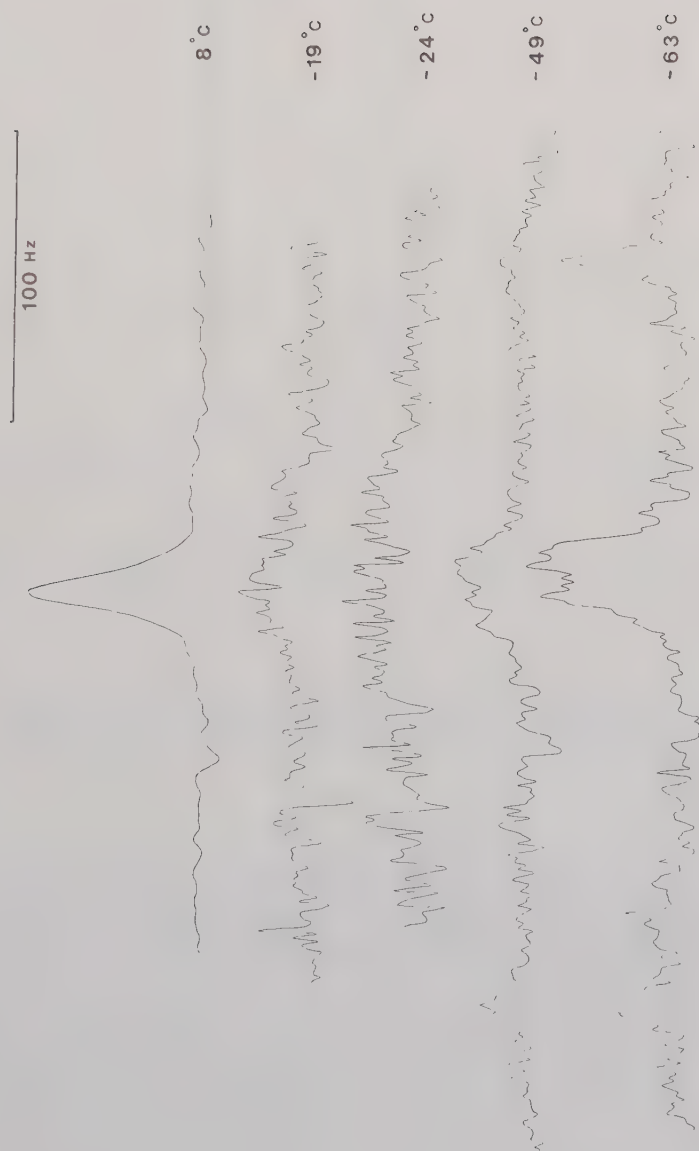


Fig. 19. Temperature dependence of the unsubstituted aromatic region in the ^{13}C NMR spectrum of compound (23) in $\text{CS}_2/\text{acetone-}d_6$ (5:1) solution.

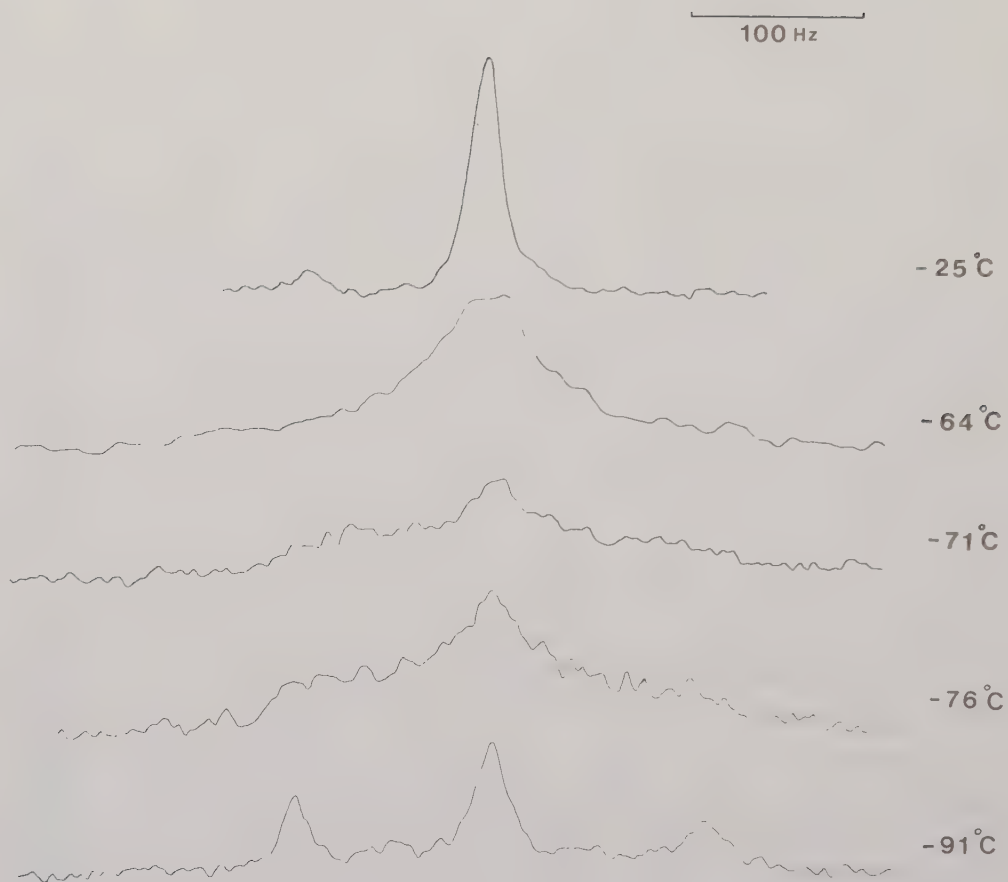


Fig. 20. Temperature dependence of the unsubstituted aromatic region in the ^{13}C NMR spectrum of compound (27) in acetone- d_6 /CS $_2$ (1:5) solution. The small peak to left (-25 °C) is an impurity.

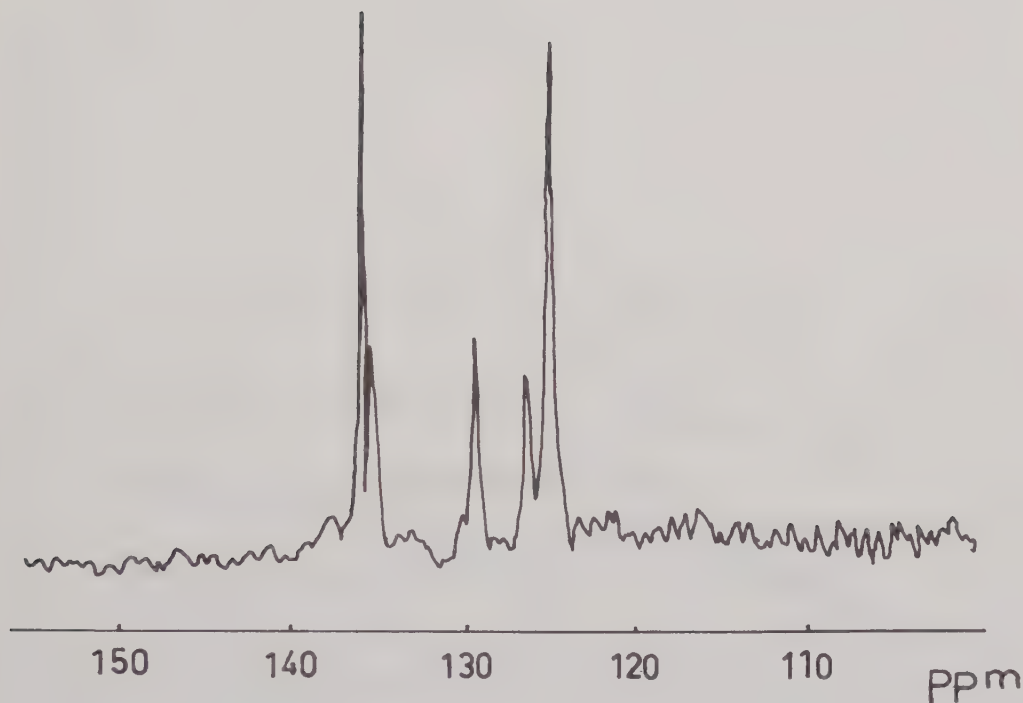


Fig. 21. Aromatic region in the ^{13}C NMR spectrum of compound (32) in acetone- d_6 : CS_2 (1:5) solution, at ambient temperature.

The aromatic carbon region in the ^{13}C NMR spectra of the achiral compound (28), (29), (31) and (33) is expected to consist of two singlets, one from the unsubstituted and one from the substituted aromatic carbons, as observed (Table 11).

The aromatic region in the spectra of the achiral compounds (29), (31) and (33) remained essentially the same down to the lowest temperatures attainable (-156°C for 29, -153°C for 31 and -125°C for 33).

^{19}F NMR measurements

The ^{19}F NMR spectrum of compound (28) in CHCl_2F solution is shown in Fig. 22. At high temperatures, when the neopentyl rotation is rapid, only one signal is expected from the benzylic fluorines, just as found. But at temperatures where the neopentyl rotation is sufficiently slow, two rotamers will exist, namely rotamer D (page 5) and rotamer A=B=C (page 5). In rotamer D, all fluorines will

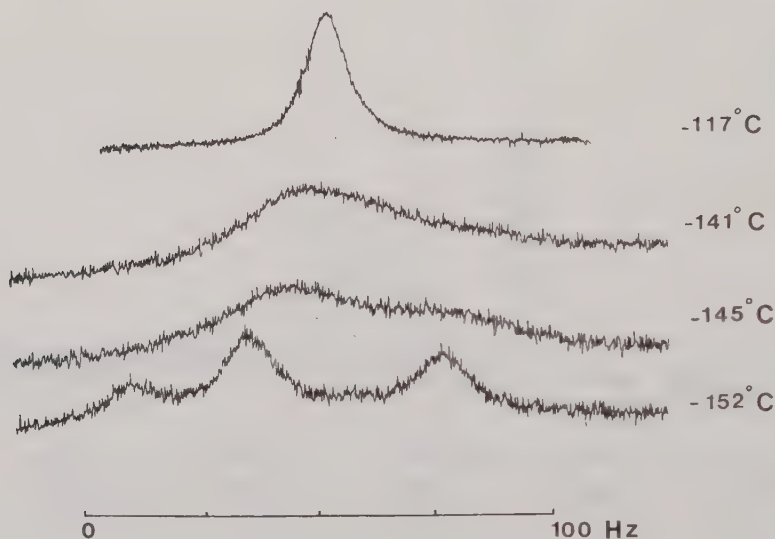


Fig. 22. Temperature dependence of the ^{19}F NMR spectrum of compound (28) in CHCl_2F solution.

of course give rise to a singlet, but in rotamer A=B=C two AB quartets will arise, with intensity ratio 1:2. Due to solubility problems at low temperatures, neither of the expected AB quartets could be resolved. However, the two outermost signals at -152°C (Fig. 22) are very broad and have the approximate intensity ratio 1:2.

To estimate $\Delta G^\ddagger_{\text{T}}$ for compounds (21)-(28), (30) and (32) an approximate band shape method involving a three-site case was used (see discussion). The values are summarized in Table 12. The signals used as internal resolution standards

TABLE 12. ^{13}C (and ^{19}F) chemical shift differences ($\Delta\nu$) and calculated free energies to activation ($\Delta G^\ddagger$) for the neopentyl rotation in some benzylic substituted TNB:s.

Compound	$\Delta\nu/\text{Hz}$	$\Delta G^\ddagger/\text{kJmol}^{-1}$	(T/ $^\circ\text{C}$) ^a	Solvent
21	28.0 $\pm$ 1.0 22.0	37.5 $\pm$ 0.9	(-86)	acetone- d_6 : CS_2 (1:5)
22	57.5 $\pm$ 1.5 35.5	41.7 $\pm$ 1.3	(-54)	"
23	147.5 $\pm$ 1.0 108.5	47.8 $\pm$ 1.1	(-24)	"
24	61.9 $\pm$ 1.5 61.0	41.1 $\pm$ 1.2	(-41)	"
25	59.0 $\pm$ 2.0 54.0	36.8 $\pm$ 1.3	(-73)	"
26	59.2 $\pm$ 1.0 38.5	36.3 $\pm$ 1.0	(-63)	"
27	115.0 $\pm$ 1.5 123.0	39.3 $\pm$ 1.0	(-64)	"
28	25.0 $\pm$ 2.0 ^b 41.0	25.8 $\pm$ 1.2	(-141)	CHCl_2F
30	62.0 $\pm$ 2.0 61.0	33.4 $\pm$ 1.2	(-91)	acetone- d_6 : CS_2 (1:5)
32	80.0 $\pm$ 2.0 56.0	37.5 $\pm$ 1.0	(-82)	"

^a Error in temperature ± 2 $^\circ\text{C}$.

^b ^{19}F chemical shift differences.

are noted in Table 11, except for compound (28), where one of the solvent (CHCl_2F) peaks was used.

VII.3 Rotation around the $\text{C}_{\text{sp}^3}-\text{C}_{\text{sp}^3}$ bond

In analogy with the case of t-butyl rotation in mono-neopentylbenzenes (chapter VI.3), the t-butyl resonances in the chiral compounds (20-27, 30 and 32) are expected to split into three signals of equal intensities, when the t-butyl rotation is sufficiently slow. However, for compounds (21)-(27) and (32) only 1:2 doublets were observed, evidently as the result of chemical shift equivalence between two of the three ^{13}C methyl resonances.

For compounds (20) and (30) the t-butyl resonances remained singlets down to the lowest temperatures attainable (-120°C for 20 and -105°C for 30).

For the achiral compounds (28), (29), (31) and (33), the t-butyl resonances are expected to split into two signals in the ratio 1:2, when t-butyl rotation is slow, because two of the three methyl groups will reside in identical chemical environments. This is also what has been observed, and is exemplified in Fig. 23 for compound (31).

Band shape analysis

To estimate the t-butyl rotation rate for compounds (21)-(29) and (31)-(33), the spectra were simulated as two-site cases with a 1:2 population ratio, and the mean life time for the low population site was used to calculate $\Delta G_{\text{T}}^\ddagger$. For the chiral compounds (21)-(27) and (32), this is a simplified treatment, but it can be justified by the same argument as given in chapter VI.3 for the treatment of the t-butyl rotation in mono-neopentylbenzenes.

The signals used as internal resolution standards are noted in Table 11.

From estimated mean life times (τ), the free energies to activation ($\Delta G_{\text{T}}^\ddagger$) were calculated. The results are summarized in Table 13.

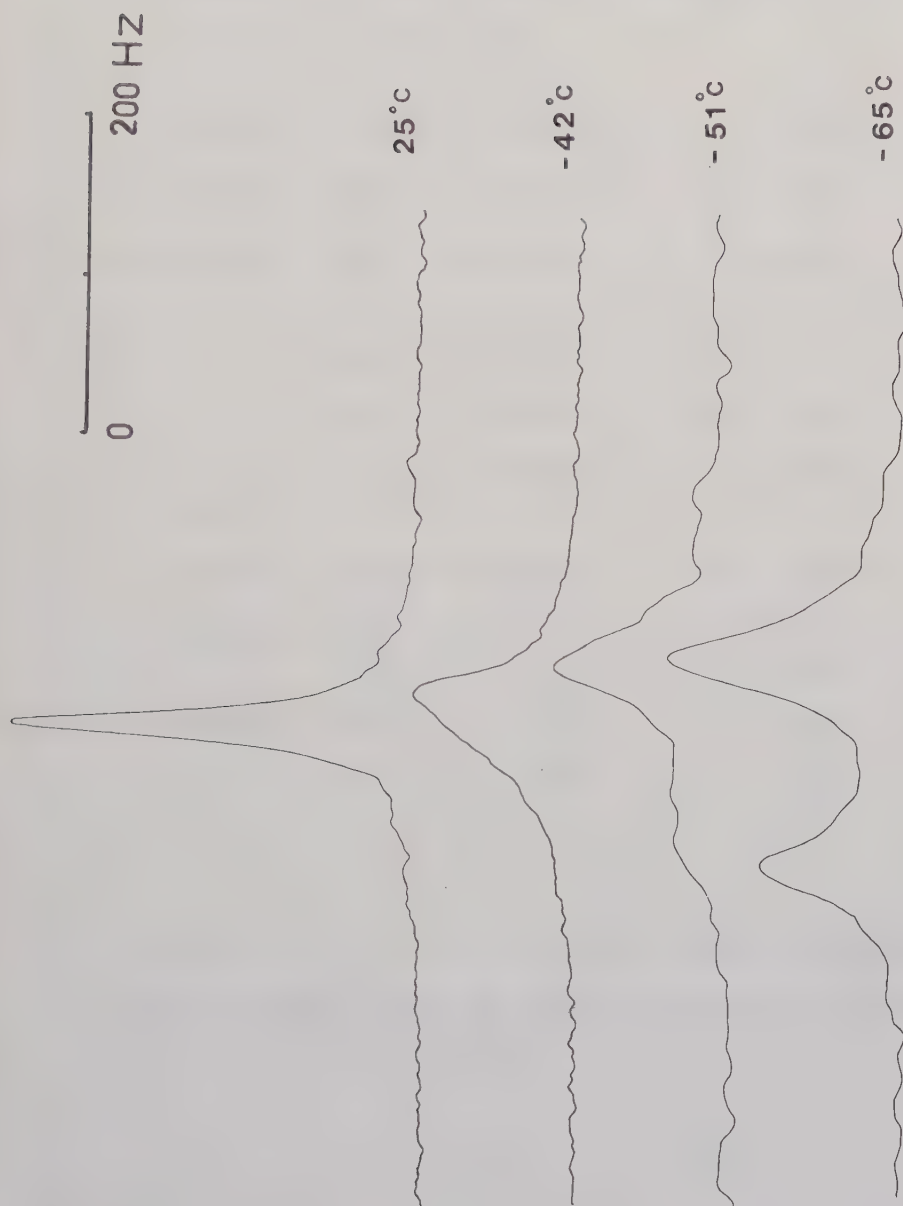


Fig. 23. Temperature dependence of the methyl resonances in the t-butyl groups in the ^{13}C NMR spectrum of compound (31) in chloroform-d solution.

TABLE 13. ^{13}C chemical shift differences ($\Delta\nu$) and calculated free energies to activation ($\Delta G^\ddagger$) for the t-butyl rotation in some benzylic substituted TNB:s.

Compound	$\Delta\nu/\text{Hz}$	$\Delta G^\ddagger/\text{kJmol}^{-1}$	(T/ $^\circ\text{C}$) ^a	Solvent
21	195.0 $\pm$ 2.5	31.8 $\pm$ 0.5	(-99)	CHCl_2F
22	90.0 ^b	35.2 $\pm$ 0.8	(-94)	acetone- d_6 : CS_2 (1:5)
23	130.0 ^b	35.3 $\pm$ 0.6	(-91)	"
24	174.0 $\pm$ 2.5	27.5 $\pm$ 0.8	(-108)	CHCl_2F
25	131.0 $\pm$ 2.0	28.4 $\pm$ 0.8	(-109)	"
26	150.0 $\pm$ 3.0	34.3 $\pm$ 1.0	(-102)	"
27	130.0 $\pm$ 2.0	27.9 $\pm$ 0.8	(-115)	acetone- d_6 : CS_2 (1:5)
28	52.0 $\pm$ 1.0	28.2 $\pm$ 0.7	(-132)	CHCl_2F
29	39.1 $\pm$ 0.6	44.9 $\pm$ 0.7	(-56)	CDCl_3
31	131.8 $\pm$ 0.8	49.7 $\pm$ 0.9	(-42)	"
32	97.7 $\pm$ 0.7	43.3 $\pm$ 1.2	(-62)	acetone- d_6 : CS_2 (1:5)
33	14.0 $\pm$ 1.5	35.9 $\pm$ 1.3	(-106)	CHCl_2F

^a Uncertainty in temperature $\pm 2^\circ\text{C}$.

^b Estimated shift differences from broadenings below coalescence, because low temperature spectra could not be obtained due to solubility problems.

VII.4 Discussion

In analogy with the work of Baas and Sinnema¹⁴⁵ on the chiral compound 1,3,5-tris(1-hydroxy-1,2,2-trimethylpropyl)benzene, it was stated in chapter VII.2 that two diastereomeric pairs are possible. One pair consists of a mixture of RRR and SSS enantiomers, while the other is a mixture of RRS and SSR enantiomers. In Fig. 24 (next page), this is exemplified for compound (23), but only one of the two possible enantiomers for each diastereomer (Ia and IIa) is shown.

The unsubstituted aromatic carbon region in the ^{13}C NMR spectrum of compound (23) at temperatures where neopentyl rotation is slow will be analyzed. An analysis of the substituted aromatic carbon region or the benzylic carbon region could also be performed, but in most cases the shift differences (in the NMR spectra) observed from these regions are smaller than those observed from the unsubstituted aromatic carbon region. The analysis is of course not restricted to compound (23), but is general for all of the chiral compounds studied (20-27, 30 and 32).

In rotamer Ia (Fig. 24), which is the SSS enantiomer, all unsubstituted aromatic carbons will have the same chemical shift ν_{IH} (because each carbon is situated between one benzylic iodine and one benzylic hydrogen).

Rotation of each of the neopentyl groups in rotamer Ia by 180° gives rise to rotamers Ib, Ic and Id. In each of these rotamers, all of the unsubstituted aromatic carbons will have different chemical shifts. One of the unsubstituted aromatic carbons in rotamers Ib, Ic and Id will have the chemical shift ν_{IH} (as in rotamer Ia) but the other two, situated between two benzylic protons or two benzylic iodines, will have the chemical shifts ν_{HH} or ν_{II} , which are upfield and downfield, respectively, relative to ν_{IH} .¹⁴⁷ It is then assumed that the chemical shift for an aromatic carbon will be the same (or there will be very little difference) if the two proximate benzylic iodines, protons or t-butyl groups are on the same or opposite sides of the ring plane.

In rotamer IIa (the SSR enantiomer), the unsubstituted aromatic carbons will have three different chemical shifts situated at ν_{II} , ν_{HH} and ν_{IH} . A 180° -rotation of the neopentyl group with the R configuration in rotamer IIa gives rise to rotamer IIb. In this rotamer, the three unsubstituted aromatic carbons will all have the same chemical shift, centered at ν_{IH} .

However, if each of the two neopentyl groups with the S configuration in rotamer IIa is rotated 180° , rotamers IIc and IId are formed. The chemical shifts for the unsubstituted aromatic carbons will all be different in both rotamers, in analogy with rotamer IIa.

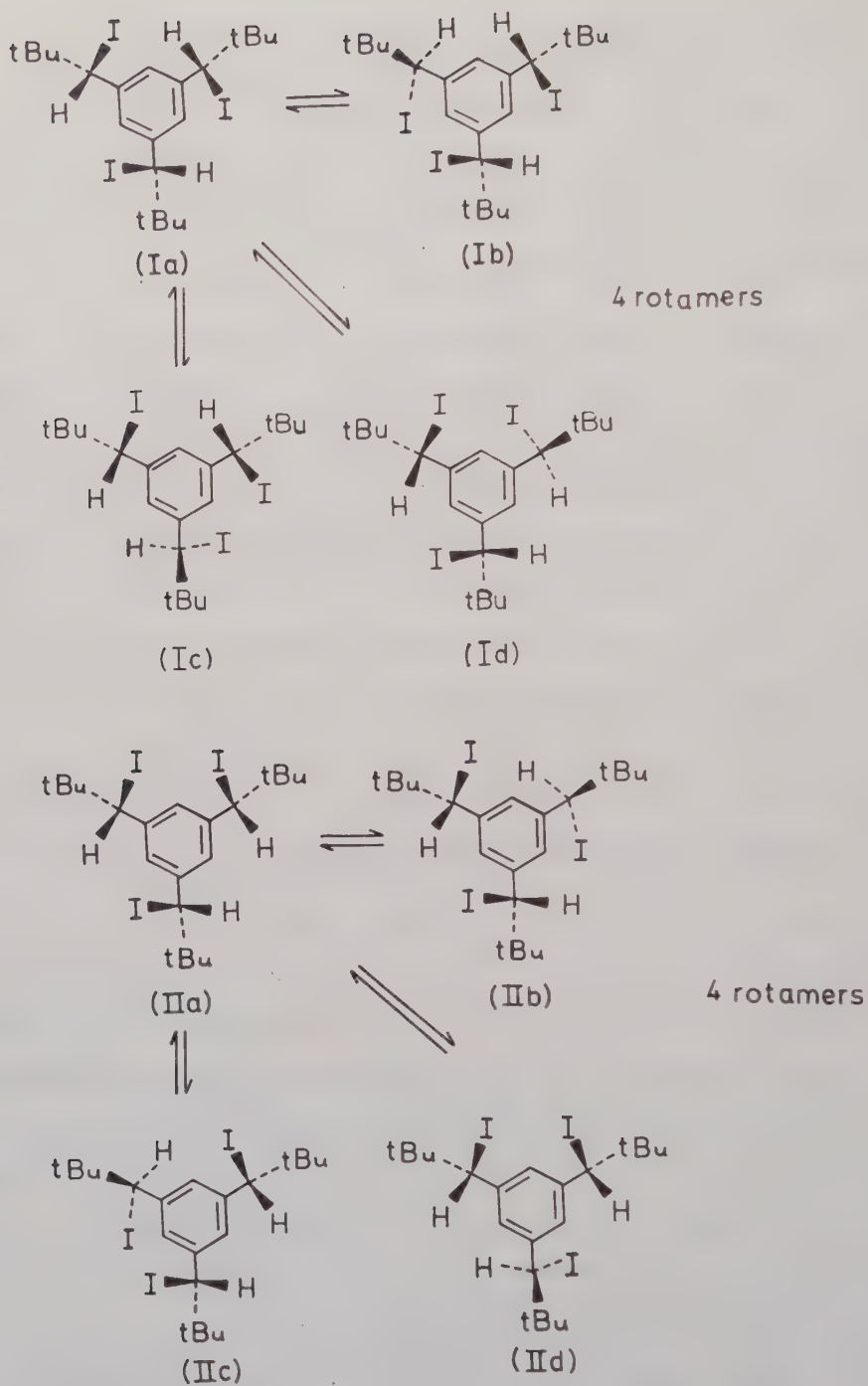


Fig. 24. Different rotamers of the SSS and SSR enantiomers of compound (23).

The net result is then six signals centered at ν_{II} , 12 at ν_{IH} and 6 at ν_{HH} . However, before we can predict the intensity ratios in the ^{13}C NMR spectrum of compound (23), the statistical probability must be taken into account. If a statistical probability of 50 % is assumed for the production of a chiral benzylic center with R configuration, there will be a 25 % total probability for the formation of the RRR and SSS enantiomers. There will then be a 75 % total probability for the formation of the RRS and SSR enantiomers. If the differential effect of t-butyl groups on opposite sides of the ring plane is neglected, the unsubstituted aromatic carbon region in the spectrum of compound (23), at temperatures where neopentyl rotation is slow, may be roughly predicted to consist of three signals centered at ν_{IH} , ν_{II} and ν_{HH} , with the relative intensities 1:2:1.

From the discussion above it is clear that a band shape method involving simulation as a three-site case should be a good approximation here. However, some restrictions on the general three-site case are necessary: i) only the exchanges $\nu_{II} \rightleftharpoons \nu_{IH}$ and $\nu_{IH} \rightleftharpoons \nu_{HH}$ are considered, and ii) no direct exchange is allowed between ν_{II} and ν_{HH} . Furthermore, the populations at sites ν_{II} and ν_{HH} will be equal. In all spectra of the chiral compounds (21-27, 30 and 32) the relative intensities 1:1.9:1 to 1:2.6:1 were found from band shape analysis. A divergence from 1:2:1 shows that not all of the rotamers in Fig. 24 are equally populated, i.e. some of them are preferred.

For the achiral compounds (29), (31) and (33) at temperatures where the neopentyl rotation is slow, the aromatic ^{13}C NMR spectrum will consist of three signals from the unsubstituted and three from the substituted aromatic carbons. This will be the result of the presence of the two rotamers D and A=B=C (page 5). In the above discussion of the chiral systems, it was assumed that the location of the halogens, hydrogens or t-butyl groups with respect to the ring plane had little or no effect on the shifts of the unsubstituted aromatic carbons. In the case of achiral compounds, this is the only effect when the neopentyl rotation is slow. It is thus not surprising that no shift effects could be detected for compounds (29), (31) and (33).

$\text{C}_{\text{sp}}\text{-C}_{\text{sp}}^2(\text{aryl})$ rotation

There is good agreement between the trends in barriers estimated for the neopentyl rotation in the TNB compounds (21)-(27) (Table 12) and the similarly substituted mono-neopentylbenzenes (6)-(12) (Table 4, chapter VI). This is expected if the steric attractive effects in the TNB system¹⁷⁻¹⁹ are left out of consideration. Tables 12 and 4 (chapter VI) show that within experimental

error the neopentyl barriers found in the two series are the same.

Nilsson *et al.*¹⁷ have estimated barriers to internal neopentyl rotation in the ring-substituted compounds 2,4-difluoro, 2,4-dichloro, 2,4-dibromo, 2,4-diiodo and 2,4-dimethylTNB. Their results are collected in Table 14, together with the results from measurements on the benzylically-substituted compounds (21)-(23) and (27).

Table 14. Barriers to internal neopentyl rotation (kJmol^{-1}) for some benzylically and ring-substituted TNB:s.

Compound	$\Delta G^\ddagger$	Compound	$\Delta G^\ddagger$
(20)	-	2,4-F ₂ -TNB	37.0
(21)	37.5	2,4-Cl ₂ -TNB	61.6
(22)	41.7	2,4-Br ₂ -TNB	69.5
(23)	47.8	2,4-I ₂ -TNB	78.7
(27)	39.3	2,4-Me ₂ -TNB	64.5

The barrier to internal neopentyl rotation in compound (20) could not be estimated from ¹³C NMR spectra. Table 14 shows that there is good agreement between the trends in the two series, although the barriers found for the benzylically-substituted TNB:s are lower than those for ring-substituted TNB:s.

In chapter VI it was stated that the neopentyl barrier decreases when a third substituent is introduced in the benzylic position. The neopentyl barriers could be estimated only for compounds (28), (30) and (32). Comparison of the $\Delta G^\ddagger$ values estimated for neopentyl rotation in compounds (21), (22), (27), (30) and (32) (Table 12), shows that if benzylic methyl groups are introduced in compounds (21) and (22), the neopentyl barriers decrease by 4.1 kJmol^{-1} from $37.5 \pm 0.9 \text{ kJmol}^{-1}$ (21) to $33.4 \pm 1.2 \text{ kJmol}^{-1}$ (30) and by 4.2 kJmol^{-1} from $41.7 \pm 1.0 \text{ kJmol}^{-1}$ (22) to $37.5 \pm 1.0 \text{ kJmol}^{-1}$ (32). When benzylic chlorines are introduced in compound (27) the barrier to neopentyl rotation decreases by 5.9 kJmol^{-1} from $39.3 \pm 1.0 \text{ kJmol}^{-1}$ (27) to $33.4 \pm 1.2 \text{ kJmol}^{-1}$ (30). If benzylic bromines are introduced a very small change is found (1.8 kJmol^{-1} ; within lower error limit), since the barrier found for compound (32) is $37.5 \pm 1.0 \text{ kJmol}^{-1}$.

Anderson *et al.*¹³¹ observed by ^1H NMR a decrease in neopentyl barriers of 5.0 and 5.8 kJmol^{-1} when the benzylic protons in para- NO_2 and para- OCH_3 -substituted 1-phenyl-1,2,2-trimethylpropane (cf. compound 12, chapter VI) were replaced by chlorines. They explained the decrease in barrier as due to the destabilisation of the initial state when the benzylic hydrogen is replaced by a chlorine (cf. chapter VI). This will then lead to a decreased barrier to internal rotation, provided the transition state is only slightly affected by the replacement. This explanation is also valid in the work of Rieker and Kessler¹⁴⁸, who observed a decreased barrier to internal rotation when tertiary protons in sterically hindered fluorenyl and triarylmethyl systems were replaced by bulkier groups such as hydroxyl and chlorine.

In order to try to get more information about compounds (28)-(32), MM calculations with the Allinger MMP1 program⁹⁵⁻⁹⁹ were performed. For all compounds, the MM calculations were performed on the rotamer with all three t-butyl groups on the same side and perpendicular to the ring plane (cf. rotamer D, page 5). For the chiral compounds (30) and (32) only the RRR (or SSS) isomer was used for calculations. One of the neopentyl groups in rotamer D was rotated 180° to a conformation corresponding to rotamers A, B and C (page 5). (For definition of the driving angle see Fig. 2, chapter V). Some points along the calculated potential curves are given for compounds (28)-(32) in Table 15, where the steric (E_{Steric}) and dipolar (E_{Dipole}) contributions to the total energy ($E_{\text{Total}} = E_{\text{Steric}} + E_{\text{Dipole}}$) are separated.

For all compounds rotamers A, B and C were found to be the most stable. In the case of compound (28) this is in accord with the results from band shape analysis, where an isomer ratio D/(A, B and C) = 2/3 was estimated. If the dipolar contribution (E_{Dipole}) to the total energy sum is subtracted, rotamer D is found (as in the case of TNB itself) to have the lowest energy for all compounds (Table 15).

The potential curve calculated for compounds (28) and (29) on rotating a neopentyl group 180° in rotamer D, has in both cases two maxima (of equal height), situated when the rotating group is twisted 24° out of the ring plane on either side. The other two neopentyls are still on the same side and perpendicular to the ring plane. For compounds (30), (31) and (32) the potential curves also have two peaks, but of unequal heights. The maximum is in all cases found when the rotating neopentyl is on the same side of the ring plane as the other two, and is twisted 33° , 35° and 38° , respectively, out of the ring plane. The calculations for compounds (28)-(32) show (Table 15) that if the dipolar contribution (E_{Dipole}) is subtracted from the total energy (E_{Total}) at each point along the potential curve, a potential curve similar to that for TNB (curve A in Fig. 3,

TABLE 15. Calculated steric energies (E_{Steric}), dipole energies (E_{Dipole}) for some conformations on the potential curve for internal neopentyl-rotation and total energy differences (ΔE_{Total}) in kJmol^{-1} for benzylically substituted TNB:s (see text).

Compound	A		B		C		D		E	
	E_{Steric}	E_{Dipole}	E_{Steric}	E_{Dipole}	E_{Steric}	E_{Dipole}	E_{Steric}	E_{Dipole}	E_{Dipole}	ΔE_{Total}
28	93.6	2.3	91.4	7.0	123.8	3.4	119.9	4.4		31.3
29	179.1	3.1	181.1	7.4	214.5	5.6	202.7	5.1		37.9
30	202.3	1.9	204.0	1.3	239.5	2.0	232.5	1.9		37.3
31	206.3	3.9	208.5	9.0	248.5	7.6	228.0	6.1		45.9
32	222.4	1.8	224.0	1.1	264.5	1.8	251.9	1.9		42.1

A: Initial state (rotamers A=B=C). For compounds (30) and (32) see text.

B: Rotamer D.

C: Transition state.

D: The rotamer with one neopentyl in the ring plane ($\phi=90$) and the other two neopentyls on the same side of the ring plane.

E: Calculated barrier.

chapter V) will be found in all cases.

In the case of compound (29) the potential curve was also calculated when one of the neopentyls on the same side of the ring plane in rotamers A, B and C was rotated 180° . A potential curve with two peaks of nearly the same height (difference only 2 kJmol^{-1}), situated when the rotating is 30° above or beneath the ring plane, was found. The barrier to internal neopentyl rotation, calculated as the energy difference between the highest and the lowest point on the potential curve, is 38 kJmol^{-1} . This is equal to the barrier calculated when one of the neopentyls in rotamer D was rotated 180° (cf. Table 15). If the dipolar contribution (E_{Dipole}) is subtracted from the total energy (E_{Total}) at each point along the potential curve, the dashed curve in Fig. 3 (chapter V) will be found here.

The energy differences (ΔE_{Total}) calculated in Table 15 may thus be regarded as the barriers to internal neopentyl rotation in compounds (28)-(32). Tables 12 and 15 show that barriers calculated for compounds (28), (30) and (32) are about $3\text{-}6 \text{ kJmol}^{-1}$ higher in energy than those measured. The calculations also show that when the benzylic methyl groups in compound (32) are replaced by the larger bromines (31), the barrier increases by 3.8 kJmol^{-1} (see Table 15). The theoretical results in chapter VI indicate that the barrier to internal $\text{C}_{\text{sp}}^3\text{-C}_{\text{sp}}^2(\text{aryl})$ rotation decreases when the effective size of the third substituent increases, and this result is experimentally verified above (cf. neopentyl barriers for compounds 27, 30 and 32). From the literature^{101,102,143,149} it is known that one of the most crucial problems with the MMP1 program is to get reliable results on halogen-substituted compounds. For monohalogenated alkanes, the MMP1 program gives acceptable results, but for compounds with two or more halogens, and especially in the case of geminal halogens, the MMP1 program does not give reliable results.^{102,149} Besides these observations, the MMP1 program does not contain constants for benzylic halogens in the expressions for the calculation of the torsional energy (E_{Torsion}) and bending energy (E_{Bend}) contributions to the total energy (E_{Total}) (see chapter IV, page 16). The torsional constant (V_3) and the bending constants (θ_0 and k_b) used have therefore been approximated to those estimated for halogenated alkanes. The constants used are given in Table 16.

TABLE 16. Torsional and bending constants used in the MMP1 program.

Torsional constants

$$E_{\text{Torsion}} = \frac{V_1}{2} (1 + \cos(w)) + \frac{V_2}{2} (1 - \cos(2w)) - \frac{V_3}{3} (1 + \cos(3w)) \text{ (kJ/mol)}$$

Angle	V_1	V_2	V_3	(kJ/mol)
$C_{sp}^2-C_{sp}^2-C_{sp}^3-F$	0.0	68.04	2.97	
" -Cl	0.0	68.04	3.35	
" -Br	0.0	68.04	3.35	

Bending constants

$$E_{\text{Bend}} = 0.02191 \cdot 4.187 k_b (\theta - \theta_0)^2 (1 + C_f (\theta - \theta_0)), C_f = -0.006 \text{ (kJ/mol)}$$

Angle	θ_0 (deg)	k_b (mdynÅ/rad ²)
$C_{sp}^2-C_{sp}^3-F$	109.2	1.22
" -Cl	109.8	0.96
" -Br	109.1	0.90

Another problem concerns the contribution of the electrostatic term (E_{Dipole}) to the total energy. The electrostatic term in the MMP1 program has the form¹⁴⁹

$$E_{\text{Dipole}} = 14.39418 \cdot 4.187 \mu_A \mu_B (\cos x - 3 \cos \alpha_A \cos \alpha_B) / r^3 d \text{ (kJ/mol)}$$

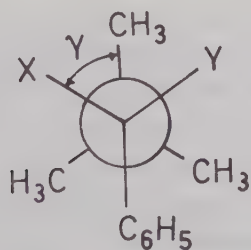
where μ_A and μ_B are bond moments, d is the dielectric constant and $\vec{r}$ is taken as connecting the midpoint of the bond that defines $\vec{\mu}_A$ with that of $\vec{\mu}_B$. The angles x , α_A and α_B are between $\vec{\mu}_A$ and $\vec{\mu}_B$, $\vec{\mu}_A$ and $\vec{r}$, $\vec{\mu}_B$ and $\vec{r}$, respectively. The bond moment factors (μ) and the dielectric constant (d) used in the program have been derived from measurements on halogenated alkanes (containing between two and six carbons) and on halogenated cyclohexanes, since experimental results are only available for these simple systems.^{102,149} In view of these limitations, the calculations of energy differences for compounds (28)-(32) must be

regarded as very approximate.

C_{sp}³-C_{sp}³-rotation

The barriers for the internal t-butyl rotation in compounds (21)-(27) (Table 13) are, as expected, equal within experimental error to those found for the corresponding mono-neopentylbenzenes (compounds 6-12, Table 6). Table 13 also shows that the barrier to internal t-butyl rotation increases as the third benzylic substituent increases in size. The t-butyl barriers found for compounds (29), (31) and (32) are in very good agreement with the results of Hawkins *et al.*¹³⁷ and those of Anderson and Pearson¹³⁸⁻¹⁴² on the internal rotation in 1,1-dihalo and 1-halo-1-methyl substituted ethanes. The t-butyl barriers observed (Table 13) are of purely steric origin, and the initial and transition states are most likely staggered and eclipsed conformations (see chapter VI). These conformations were also proposed by Hawkins *et al.*¹³⁷

The barriers to internal t-butyl rotation in compounds (28)-(32) were calculated with the MMP1 program (Table 17). In the calculations, the entire TNB molecule had the configuration of rotamer D (page 5). For the chiral compounds (30) and (32), calculations were only performed on the RRR (or SSS) isomers. The results are collected in Table 17, where the total steric energy (E_{Total} ; see pages 16 and 79) for the molecule is presented together with different values of the dihedral angle between a benzylic halogen and a methyl group in the rotating t-butyl.



X = halogen

Y = halogen or CH₃

TABLE 17. Total energy (E_{Total}), the angle (γ) between a benzylic halogen and a methyl group in the rotating t-butyl group and calculated t-butyl barriers (ΔE_{Total}) for some benzylically substituted TNB:s.

	$E_{\text{Total}}/\text{kJmol}^{-1}$				
$\gamma/^\circ$	(28)	(29)	(30)	(31)	(32)
68	-	-	204.5	-	224.4
62	98.4	188.5	205.3	217.6	225.1
52	99.2	189.6	208.2	219.2	228.2
42	101.1	192.9	210.6	222.0	230.5
32	104.8	196.7	221.5	226.2	240.3
22	108.6	202.0	214.4	232.0	236.1
12	113.5	210.1	220.5	240.6	242.1
4	116.9	216.0	227.2	246.2	248.6
1	117.7	217.4	-	248.1	-
ΔE_{Total}	19.3	28.9	22.7	30.5	24.2

As expected, the calculations show that staggered and eclipsed conformations are the initial and transition states. According to Table 17, there is a striking similarity between the trends in calculated and measured t-butyl barriers, although those calculated are much smaller. Similar discrepancies have been reported by Freitag and Schneider¹⁴³, who calculated t-butyl barriers (with the MM1 program) in monosubstituted neopentanes which are 2-6 kJmol^{-1} less than those observed from experiments. On the other hand, the MMP1 program has been reported to calculate methyl barriers (in triptycenes) that are greater than those observed experimentally¹⁵⁰, and in chapter V and VI we have seen that calculated $C_{\text{sp}}^3-C_{\text{sp}}^2(\text{aryl})$ barriers are also greater than those observed experimentally. For compound (30) the calculations of the neopentyl and the t-butyl barrier were more carefully inspected. The different energy contributions

($\Delta E_x = E_x(\text{transition state}) - E_x(\text{initial state})$) to the calculated barriers are summarized in Table 18.

TABLE 18. Different energy contributions (ΔE_x in kJmol^{-1} , see text) to the calculated $C_{sp^3}-C_{sp^2}(\text{aryl})$ and $C_{sp^3}-C_{sp^3}$ barrier in compound (30).

	$C_{sp^3}-C_{sp^2}(\text{aryl})$	$C_{sp^3}-C_{sp^3}$
$\Delta E_{\text{Compression}}$	5.8	2.6
$\Delta E_{\text{Bending}}$	8.2	7.2
$\Delta E_{\text{Stretch-bend}}$	0.5	0.3
$\Delta E_{\text{Van der Waals (vdW)}}$	14.9	10.5
$\Delta E_{\text{Torsion}}$	8.7	3.0
$\Delta E_{\text{Torsion-bend}}$	-0.7	-0.9
ΔE_{Dipole}	-0.1	-0.1

The calculations show that for t-butyl rotation, the barrier is dominated by van der Waals energy, due to interactions between the hydrogens of the t-butyl group and the surroundings, and bending energy (Table 17). For the $C_{sp^3}-C_{sp^2}(\text{aryl})$ barrier van der Waals and bending energies are still two large contributions. In addition to these energy sums, a relatively large torsional energy contribution (8.7 kJmol^{-1}) is found, due to torsion along the benzylic bond connecting the rotating neopentyl with the aromatic ring. In the case of t-butyl rotation, on the other hand, the torsional energy amounts to less than half of the bending energy. The compression energy, due to stretching forces in the twisting bonds, is also of greater importance in the case of neopentyl rotation than for t-butyl rotation.

It is difficult to predict which parameter(s) (in the MM1/MMP1 programs) should be changed in order to get theoretical results in better accord with the experimental results here. A parameter which may be very important for the results is the van der Waals radius (r_{vdW}) for the hydrogen atom, which is equal to $0.925 \cdot C-H$

bond distance in the MM1 program. The Allinger MM2 program, which uses smaller and softer hydrogens ($r_{\text{vdW}} = 0.915 \cdot \text{C-H bond distance}$), has been shown to give geometries for sterically hindered systems such as the di- and tri-*t*-butylmethane systems, which are in better accord with crystallographic data than those from the MM1 program.¹⁰¹

VIII. THE SIZE OF THE METHYL GROUP

In studies dealing with steric requirements of covalently bonded atoms or groups, the methyl group plays two special roles, according to Mislow *et al.*⁹²: "First, it provides a reference point in the spectrum of sizes for all alkyl groups. Second, it is commonly compared in size with chloro and bromo groups." The latter role of the methyl groups has received much attention, and is still a question of some interest. Many studies of the relative size of the methyl group in different molecular systems have therefore been published.^{17,92}

From the results in chapters VI and VII on substituted mono-neopentylbenzenes and TNB:s, it is possible to estimate the relative size of the methyl group in these systems. Estimated barriers to internal $C_{sp^3}-C_{sp^2}^{(aryl)}$ and $C_{sp^3}-C_{sp^3}$ rotations in the mono-neopentylbenzene system when the substituent is F, Cl, Br, I and Me are found in Tables 5 and 6 (chapter VI). In Fig. 25, these estimated

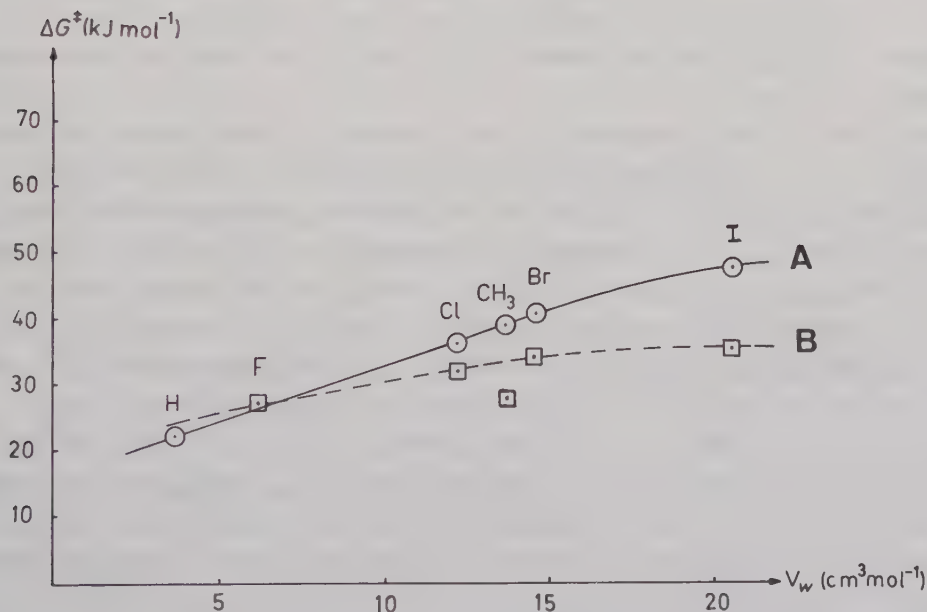


Fig. 25. The free energy ($\Delta G^\ddagger$) to neopentyl rotation (curve A) and t-butyl rotation (curve B) as a function of the van der Waals volume of the benzylic substituent in some substituted mono-neopentylbenzenes.*

* The value for the H-substituent is assumed to be the same as for TNB (chapter V).

free energies to activation ($\Delta G^\ddagger$) for internal neopentyl rotation (curve A) and for t-butyl rotation (curve B) are plotted against the van der Waals volumes for the substituents (in ethanes).^{151,152} The value found for neopentyl rotation when the benzylic substituent is CH_3 falls on curve A, but for t-butyl rotation, the value found for the CH_3 group falls under curve B. In the case of neopentyl rotation in the mono-neopentylbenzene system, the relative size of the methyl group follows the order $\text{Cl} < \text{CH}_3 < \text{Br}$, but for t-butyl rotation the relative order will be $\text{CH}_3 < \text{Cl} < \text{Br}$.

Inspection of estimated neopentyl and t-butyl barriers in the TNB system (Tables 12 and 13) when one benzylic substituent is Cl, Br, I and CH_3 reveals the relative order $\text{Cl} < \text{CH}_3 < \text{Br}$ for neopentyl rotation, while for the t-butyl rotation the order $\text{CH}_3 < \text{Cl} < \text{Br}$ is observed.

In order to get a more detailed picture of the factors that may influence the relative size of the methyl group, results from NMR studies of a variety of molecular systems are collected in Table 19.

Furthermore, from comparisons of deuterium kinetic isotopic effects in the TNB system, the size relationship $\text{CH}_3 < \text{Br}$ has been deduced.¹⁷ The relative order $\text{Cl} < \text{CH}_3 < \text{Br}$ was established from interference effects in the configurational inversion of biphenyls.¹⁵⁹⁻¹⁶¹ Taft's steric substituent constants (E_s) indicate the order $\text{Cl} < \text{Br} < \text{CH}_3$.¹⁶² Epoxidation reactions in syn-7 substituted norbornenes have been used as probes for the steric requirements of substituents with the result $\text{CH}_3 > \text{Br} > \text{Cl}$.¹⁶³

The systems in Table 19 denoted (a) are comparable, since they all represent $\text{C}_{\text{sp}}^3\text{-C}_{\text{sp}}^2(\text{aryl})$ rotations, but significant differences are only found for the systems ArCH_2X , $\text{C}_6\text{H}_5\text{CHXtBu}$ and ring and benzylically substituted TNB:s. The barriers in the $\text{C}_6\text{H}_5\text{CHXtBu}$ (mono-neopentylbenzene) and the two TNB systems have been estimated by band shape methods (from variable temperature NMR spectra), and all of these systems show the same order: $\text{Cl} < \text{CH}_3 < \text{Br}$. The barriers for the ArCH_2X system were estimated by the "J-method", i.e. from measurements of long-range coupling constants.¹²² In this system, the order $\text{CH}_3 < \text{Cl} < \text{Br}$ is found. The $\text{C}_{\text{sp}}^3\text{-C}_{\text{sp}}^2(\text{aryl})$ barriers for systems denoted (a) illustrate what has been pointed out by Nilsson *et al.*¹⁷, and by Mislow *et al.*⁹², namely that the trends depend on the molecular system involved, and the methyl, chloro and bromo groups are not strictly comparable. The chloro and bromo groups have local $\text{C}_{\infty\text{v}}$ (conical) symmetry, i.e. they are "pear shaped", whereas the methyl group has local $\text{C}_{3\text{v}}$ symmetry, i.e. it is "three pronged".

The systems in Table 19 denoted (b) involve $\text{C}_{\text{sp}}^3\text{-C}_{\text{sp}}^3$ rotations and are all comparable, since the variable substituent (X) is attached to one of the two carbons defining the bond around which rotation occurs. A clear tendency toward

TABLE 19. Estimated barriers ($\Delta G^\ddagger$) to rotation or ring inversion (kJmol^{-1}) for different molecular systems, where the substituent (X) are Cl, CH_3 and Br.

Cl	CH_3	Br		Reference
8.4 ± 0.8	5.0 ± 0.8	$> 13^a$	ArCH_2X	122,124
8.4 ± 1.2	8.2 ± 0.8	14.7 ± 2.4^a	ArCHX_2	122,124
47.7 ± 1.0	46.9 ± 1.0	53.2 ± 1.0^a	$(\text{CH}_3)_3\text{C}_6\text{H}_2\text{-CHX-C}_6\text{H}_5$	129
64.5 ± 1.2	69.5 ± 1.2	94.2 ± 1.2	Dithiocyclophanes	153,154
48.6 ± 1.2	50.2 ± 1.2	64.5 ± 1.2		
61.6 ± 0.4	64.5 ± 0.4	69.5 ± 0.4^a	Ring substituted TNB:s	8-16
36.0 ± 0.9	39.2 ± 0.5	40.9 ± 1.0^a	$\text{C}_6\text{H}_5\text{-CHX-tBu}$ (chapter VI)	-
37.5 ± 0.9	39.3 ± 1.0	41.7 ± 1.3^a	Benzylically substituted TNB:s (chapter VII)	-
72.0 ± 1.0	67.0 ± 1.0	77.4 ± 1.0	10,10-dimethyl-9-methylene-9,10-dihydroanthracenes	155
45.2 ± 0.8	41.0 ± 0.8	49.8 ± 0.5^b	$\text{CH}_3\text{CClX-C}_2\text{H}_5$	137
49.8 ± 0.5	45.2 ± 1.0	51.4 ± 0.8^b	$\text{CH}_3\text{CBrX-C}_2\text{H}_5$	137
32.4 ± 0.5	26.4 ± 0.5	34.9 ± 1.0^b	$\text{C}_6\text{H}_5\text{CHX-tBu}$ (chapter VI)	-
31.8 ± 0.5	27.9 ± 0.8	35.2 ± 0.8^b	Benzylically substituted TNB:s (chapter VII)	-
31.8 ± 1.2	33.1 ± 1.2	32.7 ± 1.2^d	tBu_3SiX	156
20	18	21^c	1,3-Dioxanes	157
44.4 ± 4.1	46.9 ± 2.2	47.7 ± 2.4^e	9-Alkyltritypcenes	158
106.7 ± 9.2	91.3 ± 4.4	$> 109^e$		
32.2 ± 0.8	28.1 ± 0.8	32.7 ± 0.8^b	$\text{CH}_3\text{CHX-tBu}$	143

^a $\text{C}_{\text{sp}}^3\text{-C}_{\text{sp}}^2$ (aryl) rotation.

^b $\text{C}_{\text{sp}}^3\text{-C}_{\text{sp}}^3$ rotation.

^c These values correspond to $\Delta H^\ddagger$ and errors are not presented.

^d Si-C rotation.

^e $\text{C}_{\text{sp}}^3\text{-C}_{\text{sp}}^3$ rotation, substituent X not attached to any of the carbons defining the rotating bond.

the order $\text{CH}_3 < \text{Cl} < \text{Br}$ is found from these systems. This result is not very surprising, since a comparison of the results of Hawkins *et al.*¹³⁷ and those of Anderson and Pearson¹³⁸⁻¹⁴² indicates that in the ethane system, the relative size of the *t*-butyl group may be smaller than that of a bromine but larger than that of chlorine. (The *t*-butyl group is much larger than the methyl group, and has the same symmetry).

The low barriers to internal rotation for methyl-substituted alkanes relative to those for chloro- and bromo-substituted alkanes have often been explained as a result of the operation of a dynamic gear effect (see discussion by Mislow *et al.*⁹²). The methyl group would enjoy an advantage with respect to the halogens, since it might be able to squeeze a proximate atom into the available space between the hydrogens, during rotation. This reduction in effective size of the methyl group would lower the activation energy.

More detailed insight into the factors producing these low barriers in methyl-substituted alkanes has been given by Freitag and Schneider¹⁴⁴ on the basis of MM-calculations on the internal *t*-butyl rotation in Cl, Br, I and Me-substituted neopentanes. When the methyl group is the substituent, they found the initial state energy of the molecule to be much higher than when the halogens are substituents, due to greater nonbonded interactions between the methyl hydrogens and the surroundings. The transition state energy was not very much different for methyl substitution than for halogen substitution. The net result will then be a smaller barrier to internal *t*-butyl rotation for the methyl-substituted compound than that for the halogen-substituted compounds.

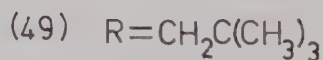
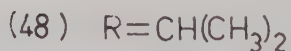
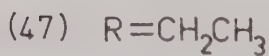
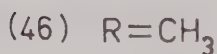
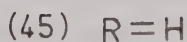
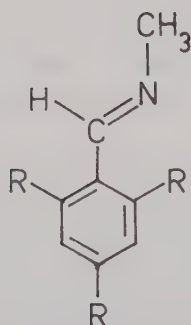
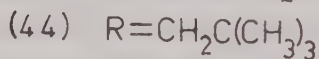
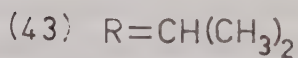
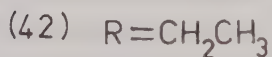
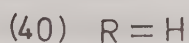
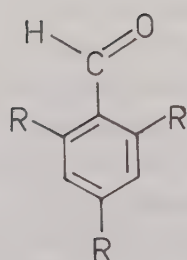
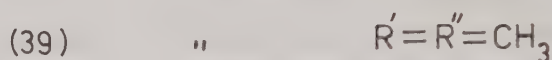
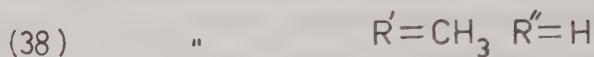
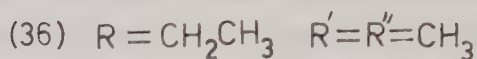
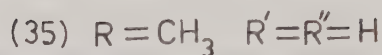
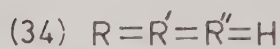
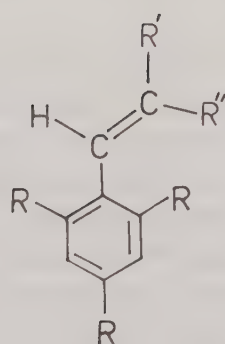
On the other hand, in the $\text{C}_{\text{sp}^3} - \text{C}_{\text{sp}^2}(\text{aryl})$ barriers the initial state for a methyl-substituted compound in many cases (depending on the molecular system) can adopt a low energy conformation, resulting in a higher barrier observed. Thus, attempts to estimate the relative size of the methyl group in relation to chlorine and bromine atoms can not provide a universally valid answer, since the relative size will depend on the system studied.

IX. 1,3,5-TRINEOPENTYLBENZENE AND RELATED 1,3,5-TRIALKYL BENZENES CONTAINING GROUPS WITH BOTH STERIC AND ELECTRONIC EFFECTS

In contrast to all studies of TNB systems containing ring and benzylic substituents with steric and dipolar (or only steric) effects, TNB:s with groups exhibiting both steric and electronic effects have rarely been studied. An exception is a paper by Dahlberg *et al.*¹¹, who studied TNB:s substituted in the aromatic ring with acyl groups. Very large differences in barriers to internal rotation were then found, ranging from 46 kJmol⁻¹ for 2-acetyl-TNB to about 96 kJmol⁻¹ for 2-pivaloyl-TNB. In the present work, vinylic groups (with different degrees of substitution in the β -vinylic position), formyl and N-methylformimino groups have been introduced into the TNB system.

The preferred conformation of unhindered aromatic ketones, aldehydes and aldimines is one in which the carbonyl (carbimino) group and the aromatic ring are coplanar.^{11,164-166} Greater and greater deviations from this coplanarity have been proposed to occur when the effective size of the ortho substituents increases.¹⁶⁵⁻¹⁶⁸ A study of some 2,4,6-trialkyl-substituted benzaldehydes and N-methylbenzaldimines was performed to determine points of similarity with the 2,4,6-trineopentyl-substituted benzaldehyde and N-methylbenzalimine systems. The compounds studied are summarized on the next page (compounds 34-49).

The studies were performed by means of ¹H NMR band shape and ¹³C relaxation time measurements. Energy barriers from NMR measurements are compared with those from MM calculations.



IX.1 Measurements and calculations

The dynamic ^1H NMR method was applied to compounds (36)-(39), but only for compounds (36) and (39) could the barrier to internal rotation be estimated. In the case of compound (36), a two-site band shape method was applied, and for compound (39) the method involved simulation as an AB case.

The ^{13}C chemical shifts for all compounds are summarized in Table 20.

The mathematical models of a) Woessner, involving a free diffusion process, and b) London and Avitabile, involving free diffusion in a restricted range, were used to calculate internal correlation times (τ_i) from measured relaxation times. The free energies to activation at ambient temperature ($\Delta G_{301}^\ddagger$), were then calculated from the τ_i by means of equation (3, see Table 21).

In equations (6) and (7) τ_α and τ_m represent the correlation times for the vinyl (formyl, formimino) group motion and the overall motion, respectively. $T_{1\alpha}$ and T_{1m} are the T_1 values for the alpha carbon in the vinyl (formyl, formimino) group and the unsubstituted aromatic carbons (in the meta positions). Measurements of the nuclear Overhauser effect (in compounds 34, 35 and 40-49) showed that the relaxation of the alpha (C- α) carbon and the aromatic C-3(5) carbons is completely dominated by dipolar relaxation. The r_α and r_m values (i.e. the carbon-proton bond distances for the alpha and the meta carbon, respectively) were taken from the MM calculations. However, as pointed out in chapter V (page 24), Stark *et al.*¹⁰³ have advised a corrected value of 1.114 Å for the aromatic hydrogen bond length (r_m) instead of the normally accepted 1.09 Å, because effects of vibrational averaging must be taken into account. The value of r_α was then corrected (+ 0.024 Å) in a manner similar to that given in chapter V. For the N-methylaldimines, the same r_α and r_m values were used as for the corresponding aldehydes. The angle β in equations (6) and (7), i.e. the angle between the internuclear (C-H) vector and the axis of internal rotation, was taken from the MM calculations, and for the N-methylaldimines the same β values were used as for the corresponding aldehydes (Table 21). The constants N_α and N_m in equations (6) and (7) are both equal to one (i.e. only one proton is bound to each of the carbons studied). The angle of diffusion (θ in equation 7) was set equal to 90° for aldehydes and N-methylaldimines, but for compound (35) it was varied. Equation (7) was solved iteratively by variation of τ_i until the equation was satisfied, and the parameter n in equation (7) was given the range ($n = 0, \dots, 100$). The calculations were performed on the UNIVAC 1100/80 at the Lund University Computing Centre.

For compounds (37) and (38) no reliable relaxation times could be obtained, due to severe overlap of the peaks of interest (Table 20).

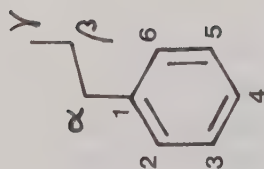


TABLE 20. ^{13}C chemical shifts (in ppm) relative to TMS for some vinyl, formyl and N-methylformyl aromats (see text).

Compound	C- α	C-1	C-2(6)	C-3(5)	C-4	other	Solvent
34	136.8	137.5	126.0	128.4	127.6	C- β =113.3	acetone-d ₆
35	137.9	137.2	137.2	131.2	137.2	C- β =121.0, o-CH ₃ =p-CH ₃ =23.7	"
36	123.0	127.6	142.8	125.2	135.2	C- β =134.2, trans-C- γ =19.6, cis-C- γ =25.3 o-CH ₂ CH ₃ =27.2, p-CH ₂ CH ₃ =27.2, o-CH ₂ CH ₃ =15.2 p-CH ₂ CH ₃ =15.4	CDCl ₃
37	138.6	138.2	136.6	131.4	136.3	C- β =119.2, o-CH ₂ tBu=46.0, p-CH ₂ tBu=50.1, o-CH ₂ C(CH ₃) ₃ =33.5, p-CH ₂ -C(CH ₃) ₃ =32.2, o-CH ₂ C(CH ₃) ₃ =p-CH ₂ C(CH ₃) ₃ =30.0	"
38	135.8	136.7	137.0	131.3	136.3	C- β =129.3, trans-C- γ =18.4, o-CH ₂ tBu=46.0 p-CH ₂ tBu=50.1, o-CH ₂ C(CH ₃) ₃ =33.5, p-CH ₂ C(CH ₃) ₃ =32.1, o-CH ₂ C(CH ₃) ₃ =p-CH ₂ C(CH ₃) ₃ =29.5	"
39	126.1	132.8	137.0	131.0	136.5	C- β =135.5, trans-C- γ =19.3, cis-C- γ =25.0, o-CH ₂ tBu=46.3, p-CH ₂ tBu=50.2, o-CH ₂ C(CH ₃) ₃ =33.3, p-CH ₂ C(CH ₃) ₃ =32.0, o-CH ₂ C(CH ₃) ₃ =p-CH ₂ C(CH ₃) ₃ =29.7.	"

40	192.1	136.0	129.5	128.8	134.3	-	CDCl ₃
41	192.5	135.4	141.2	130.3	143.6	o-CH ₃ =20.2, p-CH ₃ =21.4	"
42	192.3	130.2	147.7	127.7	149.8	o-CH ₂ CH ₃ =26.7, p-CH ₂ CH ₃ =28.8, o-CH ₂ CH ₃ =16.5, p-CH ₂ CH ₃ =14.4	"
43	194.7	130.3	150.2	121.5	153.5	o-CH(CH ₃) ₂ =28.8, p-CH(CH ₃) ₂ =34.7, o-CH(CH ₃) ₂ =24.3, p-CH(CH ₃) ₂ =23.8	"
44	194.4	136.1	141.2	133.4	142.8	o-CH ₂ tBu=44.4, p-CH ₂ tBu=50.1, o-CH ₂ C(CH ₃) ₃ =32.9, p-CH ₂ C(CH ₃) ₃ =32.2, o-CH ₂ C(CH ₃) ₃ =p-CH ₂ C(CH ₃) ₃ =29.8	"
45	162.4	136.3	128.5	128.0	130.4	N-CH ₃ =48.1	"
46	162.4	135.6	137.3	129.1	138.6	N-CH ₃ =49.4, o-CH ₃ =20.7, p-CH ₃ =21.2	"
47	161.9	131.1	143.7	126.4	144.9	N-CH ₃ =49.1, o-CH ₂ CH ₃ =26.6, p-CH ₂ CH ₃ =28.0, o-CH ₂ CH ₃ =p-CH ₂ CH ₃ =15.7	"
48	162.7	131.6	146.8	120.7	149.3	N-CH ₃ =49.0, o-CH(CH ₃) ₂ =29.5, p-CH(CH ₃) ₂ =34.5, o-CH(CH ₃) ₂ =p-CH(CH ₃) ₂ =24.0	"
49	165.3	137.9	137.3	132.4	138.2	N-CH ₃ =50.5, o-CH ₂ tBu=45.2, p-CH ₂ tBu=50.1, o-CH ₂ C(CH ₃) ₃ =33.2, p-CH ₂ C(CH ₃) ₃ =32.2, o-CH ₂ C(CH ₃) ₃ =p-CH ₂ C(CH ₃) ₃ =29.5	"

TABLE 21. T_1 values ($T_{1\alpha}$, T_{1m} and T_{1p})^a, calculated correlation times (τ_α , τ_m and τ_i)^b, geometrical angles (β), angles of diffusion (θ) and calculated free energies of activation ($\Delta G_{301}^\ddagger$).

Compound	$T_{1\alpha}/s$	T_{1m}/s	T_{1p}/s	$\tau_\alpha/10^{-12}s$	$\tau_m/10^{-12}s$	$\beta/^\circ$	$\theta/^\circ$	$\tau_i/10^{-12}s$	$\Delta G_{301}^\ddagger/kJmol^{-1}$	T_{1m}/T_{1p}
34	19.4 ± 1.0	16.6 ± 0.5	13.2 ± 0.6	2.68 ± 0.14	3.19 ± 0.10	63	-	$23.4-70.5$	$12.4-15.2$	1.3 ± 0.1
35	20.2 ± 1.0	6.01 ± 0.20	-	2.57 ± 0.14	8.83 ± 0.29	63	82-106	1.0	4.6	-
40	14.3 ± 0.6	10.6 ± 0.4	7.64 ± 0.50	4.01 ± 0.19	5.01 ± 0.20	64.7	90	$27.0-60.8$	$12.8-14.9$	1.4 ± 0.1
41	5.66 ± 0.35	3.55 ± 0.23	-	10.2 ± 0.7	20.1 ± 1.9	66.9	90	$32.0-82.0$	$13.3-15.6$	-
42	4.30 ± 0.24	2.19 ± 0.10	-	13.4 ± 0.7	24.2 ± 1.2	63.4	90	$27.0-45.0$	$12.8-14.7$	-
43	6.80 ± 0.50	1.69 ± 0.07	-	8.46 ± 0.72	89.7 ± 3.7	65.0	90	$1.0-4.62$	$4.5-8.4$	-
44	1.43 ± 0.09	0.59 ± 0.03	-	40.2 ± 2.7	90.0 ± 5.0	65.6	90	$47.0-85.0$	$14.2-15.7$	-
45	7.45 ± 0.36	6.98 ± 0.23	4.60 ± 0.33	7.72 ± 0.39	7.60 ± 0.26	64.7	90	^c	^c	1.5 ± 0.3
46	8.79 ± 0.60	3.65 ± 0.13	-	6.54 ± 0.48	14.5 ± 0.6	66.9	90	$8.2-14.5$	$9.9-11.3$	-
47	7.70 ± 0.60	2.40 ± 0.10	-	7.47 ± 0.63	22.1 ± 0.9	63.4	90	$3.6-8.5$	$7.8-10.0$	-
48	3.80 ± 0.20	1.36 ± 0.07	-	15.1 ± 0.8	39.1 ± 2.0	65.0	90	$12.6-23.0$	$10.9-12.4$	-
49	1.50 ± 0.20	0.90 ± 0.06	-	38.3 ± 5.8	59.0 ± 5.7	65.6	90	$79.0-280$	$15.5-18.7$	-

^a $T_{1\alpha}$, T_{1m} and T_{1p} refer to T_1 value for alpha carbon, aromatic meta and aromatic para carbon and the errors are

all 3 σ (see text). ^b τ_α , τ_m and τ_i are the correlation times for alpha carbon, molecular and internal correlation times resp. (see text). ^c Could not be estimated.

TABLE 22. Calculated total energies (E_{Total}) for different conformations along the potential curve and calculated barriers to internal rotation (ΔE_{Total}).

Compound	$E_{\text{Total}}^a / \text{kJmol}^{-1}$	$E_{\text{Total}}^b / \text{kJmol}^{-1}$	$E_{\text{Total}}^c / \text{kJmol}^{-1}$	$\Delta E_{\text{Total}} / \text{kJmol}^{-1}$
34	48.4	-	58.7	10.3
35	65.8	-	91.7	25.9
36	95.8	98.1	159.8	64.0
37	113.1	127.5	164.5	51.4
38	115.1	127.3	175.9	60.8
39	117.8	126.2	195.0	77.2
40	36.7	-	55.9	19.2
41	53.8	-	62.0	8.2
42	79.9	-	82.3	2.4
43	105.2	-	116.7	11.5
44	108.0	-	115.1	7.1

^a The most stable conformer, for compounds (36)-(39), (42) and (44) the conformer with all three alkyl groups on one side of the ring plane and the vinyl (formyl) group on the other side of the ring plane.

^b The conformer with one ortho alkyl group and the vinyl group on one side of the ring plane and the other two alkyl groups on the other side. ^c The conformer which corresponds to the highest point on the potential curve (see text).

The Allinger MMP1 program⁹⁵⁻⁹⁹ was used to calculate the total energy (E_{Total}) for different conformations on the potential surface for internal rotation of the vinyl (formyl) group in compounds (34-44, see Table 22). However, the program has no parameters suitable for calculations on aldimines. The calculations were performed for compounds (34), (35), (37), (38) and (40)-(44) by driving the vinyl (formyl) group 180° (in increments of 5°) around the $C_{\text{sp}^2}-C_{\text{sp}^2}(\text{aryl})$ bond from the initial state, while all other groups in the molecule were free to relax. In the calculations of compounds (36) and (39), where experimental evidence for restricted rotation was observed, the ortho alkyl group, toward which the vinyl was rotated, was also driven to give the conformation of lowest energy (for each rotation of the vinyl group). The other two alkyl groups in the ring were free to relax. The resulting rotational barriers are the differences between the highest and lowest points on the potential curves.

IX.2 Discussion of systems with vinylic groups

Styrene (34) is an extensively studied molecule, and barriers to internal rotation found in the literature show considerable variation.^{46,97,164,169-173} NMR measurements give barriers in the interval 6.7-16.2 kJmol^{-1} , while microwave spectroscopic methods give 2.1-9.2 kJmol^{-1} , and theoretical calculations give values between 6-19 kJmol^{-1} , depending on the method of calculation.

MM calculations on styrene (34) give a barrier of 10.3 kJmol^{-1} (Table 22). The lowest energy conformer has the vinyl group 30° above (below) the ring plane, and the point of highest energy occurs when the vinyl group is perpendicular to the aromatic ring, as previously reported by Allinger and Sprague.⁹⁷ The calculations also show that the coplanar conformer lies 3.6 kJmol^{-1} above the lowest point of energy. From the MM calculations it is obvious that the restricted diffusion model of London and Avitabile⁵⁶ (eqn. 7) is not valid here, as this case is an exchange among four equivalent sites. Since the barrier is low, it is however probable that the free diffusion model of Woessner⁵³ (eqn. 6) will be applicable. The barrier thus estimated from relaxation measurements is 12.4-15.2 kJmol^{-1} (Table 21).

When the ortho protons are replaced by methyl groups, as in the case of vinyl-mesitylene (35), a very low barrier to internal rotation of the vinyl group of 4.6 kJmol^{-1} (Table 21) is found from relaxation data by application of equation (7) (the restricted diffusion model⁵⁶). In the calculations, τ_i in equation (7) was set equal to 10^{-12} s as a lower limit, because lowering the τ_i value 10^{-12} s for a fixed diffusion angle Θ will only have negligible effects on calculated

T_1 -values. θ in equation (7) was then varied until the equation was satisfied.

MM calculations on vinylmesitylene give a barrier to internal rotation as high as 25.9 kJmol^{-1} (Table 22), but the potential curve shows that the transition and initial states for vinylmesitylene (35) are not the same as for styrene (34). For vinylmesitylene the initial state conformation occurs when the vinyl group is perpendicular to the ring plane, and the transition state occurs when the vinyl group lies in the ring plane.

The ^1H NMR spectra of compounds (37) and (38) in CDCl_3 solution at ambient temperature (28°C) show in each case only two singlets in the ratio 2:1 (from low field) in the methylene region. The substances were therefore dissolved in CHCl_2F and the temperature was lowered as far as possible (-135°C for compound 37 and -128°C for compound 38). No temperature effect on the methylene region could be observed in either case.

Attempts to make use of the ASIS effect (Aromatic Solvent Induced Shift)¹⁷⁴ by use of ortho dichlorobenzene (37) and hexafluorobenzene (38) gave no visible effects in the corresponding 100 MHz ¹H NMR spectra.

As mentioned earlier, no useful information could be obtained from relaxation data on substances (37) and (38). In the ^{13}C NMR spectrum of compounds (37) and (38), the vinylic alpha carbon signal overlaps with the vinyl-substituted aromatic carbon and the para aromatic carbon signal, respectively (Table 20).

The barriers calculated by the MMP1 program are 51.4 (37) and 60.8 (38) kJmol⁻¹ (see Table 22). The calculations show in both cases that the initial state conformation occurs when all neopentyl groups are on the same side of the ring plane (perpendicular to the ring) and the vinyl group is on the other and perpendicular to the ring plane. The transition state conformation occurs in both cases when the vinyl group lies in the ring plane. In this conformation one of the ortho neopentyls (in Fig. 26 the one defined by carbons 19-23) has twisted so the dihedral angle 1-6-19-20 is 85°, while the other two neopentyls remain essentially in their initial state positions.

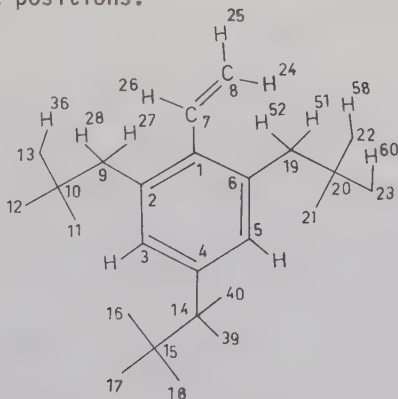


Fig. 26. Numbering in the molecular system of compound (37).

The barriers calculated for compounds (37) and (38) are in striking contrast to experimental results, since barriers as high as $50\text{-}60\text{ kJmol}^{-1}$ would easily be observable by ^1H NMR (as restricted internal rotation), unless shift equivalence occurs. However, in chapters V, VI and VII it was shown that barriers calculated by the MMP1 program on sterically strained systems deviate considerably from experimental ones. A reason for these discrepancies was suggested to be the "hard hydrogens" used in the MMP1 program. During the preparation of this chapter a version of the Allinger MMP2 program¹⁰¹ became available.¹⁷⁵ The MMP2 program uses "smaller and softer hydrogens" (see chapter VII page 85). The initial and transition states for compounds (37) and (38) were recalculated with the MMP2 program. The calculated barriers are 23.9 (37) and 18.4 (38) kJmol^{-1} (the lower barrier for compound 38 is a result of a more strained initial state). Energy contributions ($\Delta E_x = E_x(\text{transition state}) - E_x(\text{initial state})$) to the calculated barrier in compound (37) are shown in Table 23 for the two programs.

TABLE 23. Energy contributions ($\Delta E_x = E_x(\text{TS}) - E_x(\text{IS})$, in kJmol^{-1}) to the barrier in compound (37) calculated by the MMP1 and MMP2 programs.

ΔE_x	MMP1	MMP2
$\Delta E_{\text{Compress}}$	6.1	4.4
$\Delta E_{\text{Bending}}$	36.8	22.9
$\Delta E_{\text{Stretch-bend}}$	1.0	0.9
$\Delta E_{\text{van der Waals}}$	28.3	20.8
$\Delta E_{\text{Torsion}}$	-20.3	-25.1
$\Delta E_{\text{Torsion-bend}}$	-0.5	*
ΔE_{Dipole}	0	0
ΔE_{Total}	51.4	23.9

* The Torsion-bend term does not exist in the MMP2 program.

Table 23 shows that the greatest differences between the two programs are found in the bending and the van der Waals terms. The bending term has different expressions in the two programs (see Table 24).

TABLE 24. Expressions and parameters used by the MMP1 and MMP2 programs in the calculations of the bending energies in compound (37).

$$\text{MMP1: } E_{\text{Bending}} = 4.187 \cdot 0.02191 \, k_B (\theta - \theta_0)^2 (1 - 0.006(\theta - \theta_0)) \quad \text{kJmol}^{-1}$$

$$\text{MMP2: } E_{\text{Bending}} = 4.187 \cdot 0.02191 \, k_B (\theta - \theta_0)^2 (1 + 0.007 \cdot 10^{-5} (\theta - \theta_0)^4) \quad "$$

Angle	$\theta_0 (^{\circ})$	MMP1 $k_B (\text{mdyn}\text{\AA rad}^{-2})$	$\theta_0 (^{\circ})$	MMP2 $k_B (\text{mdyn}\text{\AA rad}^{-2})$
$\text{C}_{\text{sp}}^2\text{-C}_{\text{sp}}^2\text{-C}_{\text{sp}}^2$	120.0	0.60	120.0	0.43
$\text{C}_{\text{sp}}^2\text{-C}_{\text{sp}}^2\text{-H}$	120.0	0.24	120.0	0.36
out of plane	0.0	0.05	0.0	0.05
$\text{C}_{\text{sp}}^2\text{-C}_{\text{sp}}^3\text{-C}_{\text{sp}}^3$	110.2	0.38	109.5	0.45
$\text{C}_{\text{sp}}^2\text{-C}_{\text{sp}}^2\text{-C}_{\text{sp}}^3$	121.7	0.38	120.0	0.55
$\text{C}_{\text{sp}}^2\text{-C}_{\text{sp}}^3\text{-H}$	108.5	0.24	109.4	0.36
$\text{C}_{\text{sp}}^3\text{-C}_{\text{sp}}^3\text{-C}_{\text{sp}}^3$	109.5	0.38	109.5	0.45
$\text{C}_{\text{sp}}^3\text{-C}_{\text{sp}}^3\text{-H}$	108.5	0.24	110.0	0.36
$\text{H-C}_{\text{sp}}^3\text{-H}$	110.8	0.19	109.4	0.32

The differences in van der Waals energies between the two programs (Table 23) is, as pointed out above, a result of a change in the van der Waals radius for hydrogens from $0.925 \cdot \bar{r}_{\text{C-H}}$ (MMP1) to $0.915 \cdot \bar{r}_{\text{C-H}}$ (MMP2) Å. In compounds like (37) and (38) there are many interactions which together accumulate to yield large effects.

The ^1H NMR spectrum of compound (36) in CDCl_3 solution at -16°C showed a complex pattern in the methylene region, which could be interpreted as a quartet

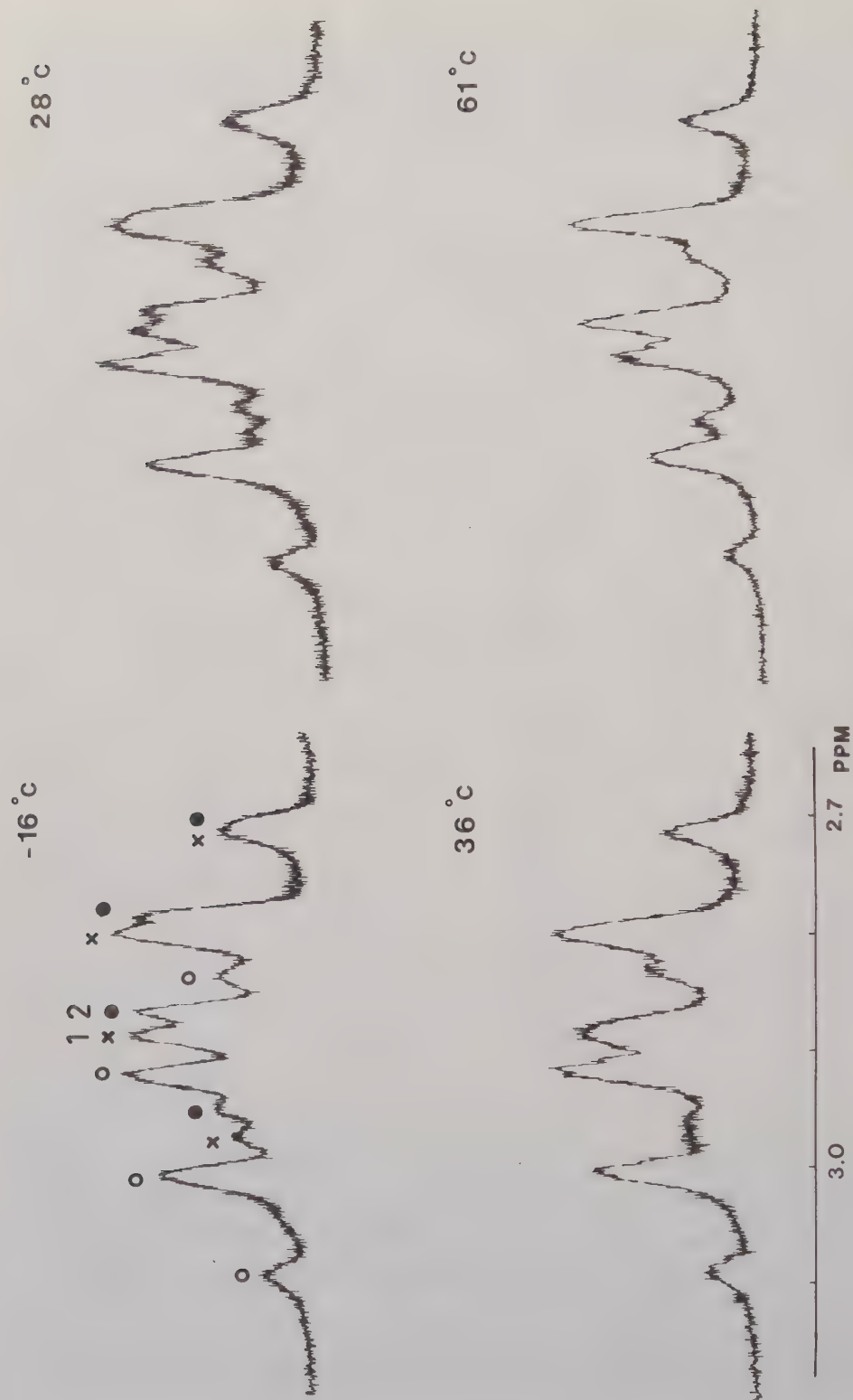


Fig. 27. The methylene region in the ^1H NMR spectrum of compound (36) in chloroform- d solution at different temperatures. Peaks belonging to the different AB quartets are marked (o, •, x) and peaks numbered 1 and 2 were used for band shape analysis.

from the p-methylene and a second quartet from the o-methylenes, which were further split due to the nonequivalence of the o-methylene protons (Fig. 27). On increasing the temperature, the latter AB quartets coalesced, and above 40 °C the methylene proton region consisted of two quartets, one from the methylene protons in the two ortho ethyl groups and the other from the methylene protons in the para ethyl group. The conditions for decoupling of the methylene resonances were not feasible (two methyl resonances must be irradiated by the spin-decoupler at the same time), and in order to get a reasonable estimate of the rate constant (τ^{-1}), the central peaks in the different AB spectra (marked 1 and 2 in Fig. 27) were used for band shape analysis, involving a two-site simulation. Due to serious overlap between signals, only an approximate rate constant could be obtained ($\tau=0.3$ s) at 29 °C, and the enthalpy and entropy terms not be estimated (Table 25).

TABLE 25. Activation parameters (from band shape analysis) for the 2-(2,2-dimethylvinyl)-1,3,5-trialkylbenzenes (36) and (39) (see text).

Compound	$\Delta G^\ddagger/\text{kJmol}^{-1}$	$\Delta H^\ddagger/\text{kJmol}^{-1}$	$\Delta S^\ddagger/\text{Jmol}^{-1} \text{ deg}^{-1}$
(36)	66 ± 3^a	-	-
(39)	74 ± 2^b	59 ± 5	$- 46 \pm 12$

^a This value corresponds to $\Delta G^\ddagger$ at 29 °C

^b This value corresponds to $\Delta G^\ddagger$ at 25 °C

The methylene region in the ^1H NMR spectrum of compound (39) in deuterio-bromoform solution at ambient temperature consists of an AB quartet from the ortho-methylene groups superimposed on a singlet from the para-methylene group (Fig. 28). As the temperature was increased, the AB quartet broadened and coalesced at about 90 °C, and at 180 °C the methylene region consisted of two sharp singlets in the ratio 2:1. The width of the singlet due to the CH_2 group para to the vinyl group was found to be independent of temperature, and a complete band shape analysis was performed (including the impurity peak; in Fig. 28), in which the singlet from the para CH_2 group was used as internal resolution standard. The free energy of activation $\Delta G_{298}^\ddagger$ and the enthalpy and entropy terms were estimated (Table 25).

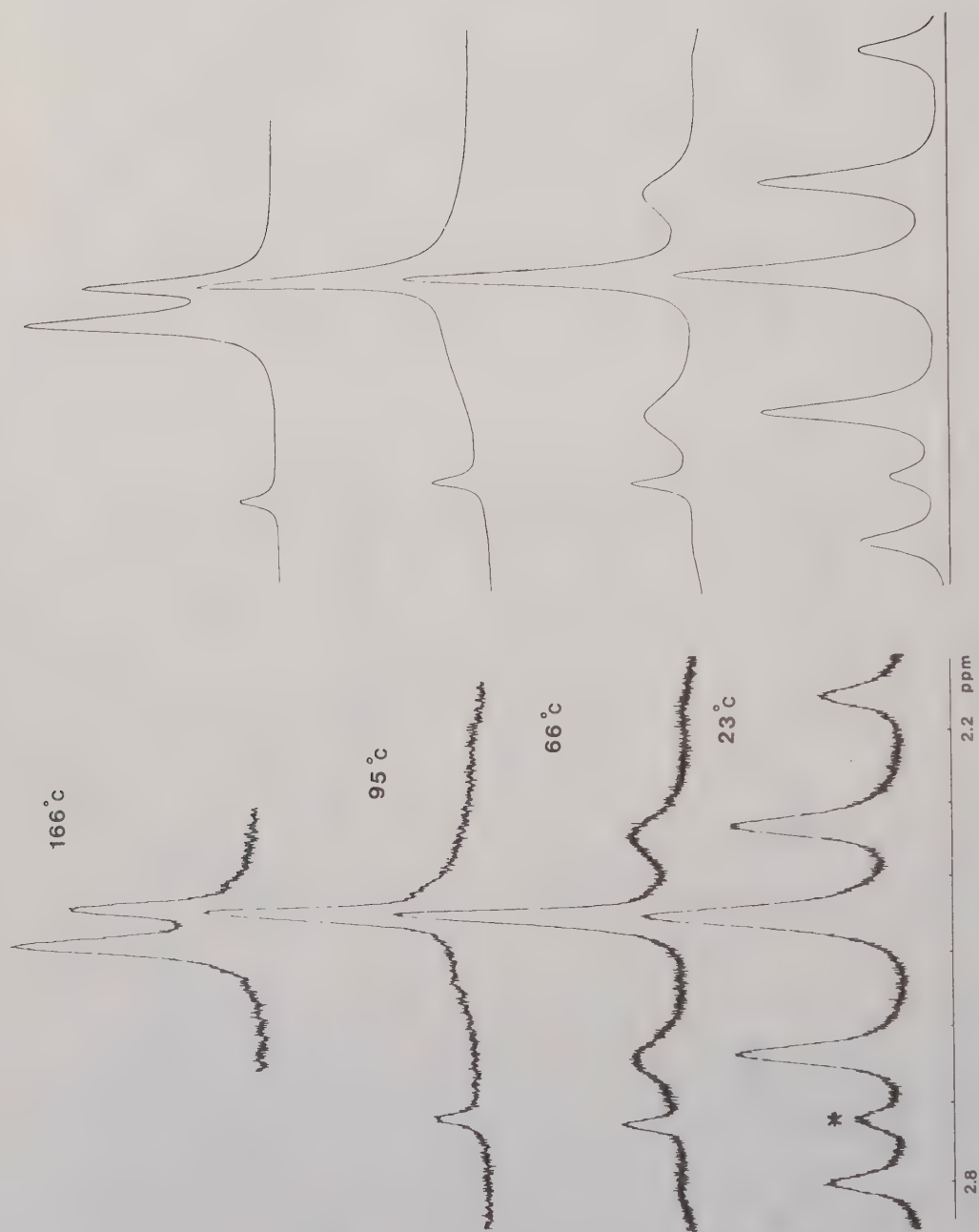


Fig. 28. Temperature dependence of the methylene region in the ^1H NMR spectrum of compound (39) in bromoform- d solution (left). The extra small peak (*) is due to an impurity and is included in the calculated spectra (right).

MM calculations on compounds (36) and (39) show the same initial state conformation as found for compounds (37) and (38). The transition state for compounds (36) and (39) was found when the vinyl group lies in the ring plane and the ortho alkyl, toward which the vinyl rotates, had rotated 90° from its initial state (angle 1-6-19-20 in Fig. 26 is 180°). Tables 22 and 23 show that there is good agreement between measured and calculated (MMP1) barriers. Initial and transition states for compound (39) were recalculated with the MMP2 program in order to check the results for a case where MMP1 calculations are in agreement with experimental data. The calculated barrier is 76.2 kJmol^{-1} (MMP2), which is in good agreement with measurements and MMP1 calculations. The MMP2 program uses a refinement of the force field from MMP1, and it seems to give results that are more realistic, at least for hydrocarbons (cf. results for compounds 37 and 38 on page 100).

IX.3 Discussion of systems with formyl groups

The restricted diffusion model⁵⁶ (equation 7) was used to treat the results from ^{13}C relaxation measurements on compounds (40)-(44) (Table 21). In performing these calculations, the maximum diffusion range of the formyl group was restricted from -90° to $+90^\circ$ (i.e. $\Theta = 90^\circ$ in equation 7). Barriers calculated with the MMP1 program are collected in Table 22 (Fig. 29).

Benzaldehyde (40) is the most extensively studied molecule of the aldehydes (40)-(44), and the literature contains a considerable range of estimated barriers to internal rotation, depending on the method used.^{98,164,176-180} Microwave and infrared measurements give values in the range $19.5\text{--}20.6 \text{ kJmol}^{-1}$, NMR methods give $31.8\text{--}33.0 \text{ kJmol}^{-1}$, and calculations $19.3\text{--}27.6 \text{ kJmol}^{-1}$ depending on the calculation method used. The value calculated in this work for benzaldehyde (19.2 kJmol^{-1}) falls into the region found in literature, but the value estimated from ^{13}C relaxation measurements ($12.8\text{--}14.9 \text{ kJmol}^{-1}$) is somewhat low. It must be remembered that all relaxation time measurements are affected by librational motions. As pointed out in chapter III.4, librational effects cause T_1 -values to be somewhat too large, which in turn will give barriers estimated to be too small.^{66,68-71} Although the exact magnitude of the librational effect in benzaldehyde is not known, its influence will be demonstrated. Suppose we allow an librational angle of 20° (Θ_{6178} in Fig. 29A varies in the range $90 \pm 20^\circ$). According to Fig. 29A an angle of 20° corresponds to an energy of 2.5 kJmol^{-1} (i.e. equal to RT , the thermal energy available at room temperature, $T = 300\text{K}$). Inserting this angle into equation 7 and assuming free libration ($\tau_l = 10^{-12} \text{ s}$)

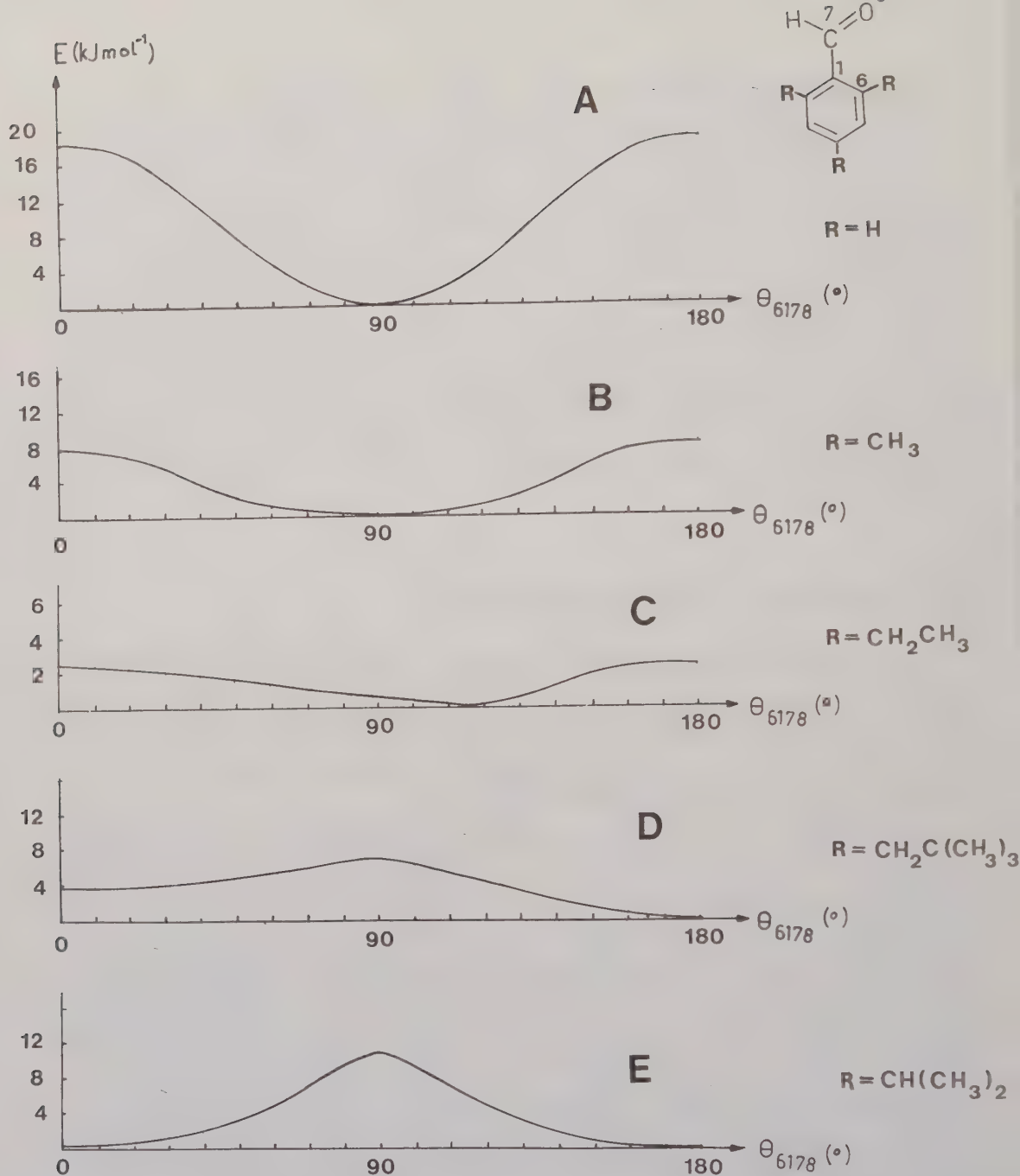


Fig. 29. Calculated potential curves for formyl group rotation in A: benzaldehyde, B: 2,4,6-trimethylbenzaldehyde, C: 2,4,6-triethylbenzaldehyde, D: 2,4,6-triisopentylbenzaldehyde and E: 2,4,6-triisopropylbenzaldehyde (for further details see text). The dihedral angle θ_{6178} is defined so that for $\theta = 0^\circ$ and 180° the formyl group is perpendicular to the ring plane.

gives a new T_{1m} value ($T_{1m}^{corr} = 11.90$ s). If T_{1m}^{corr} and $\theta = 90^\circ$ are inserted into equation 7, a new τ_i value ($= 82.5 \cdot 10^{-12}$ s) can be calculated for the absence of librational effects. The barrier to internal rotation in benzaldehyde will then be 15.6 kJmol^{-1} . The choice of a librational angle of 20° gives a decrease in rotational barrier of 12 %, which is reasonable in view of the results of Johnson⁷¹, who calculated an increase of 10% in methyl barrier in solids in the absence of these motions. It can thus be stated that librational motions must be taken into account if relaxation data are used to calculate rotational barriers.

Measured barriers for compounds (40)-(42) show no differences (within error limits), but the calculated barriers show a decrease as the ortho substituents change from H to Me to Et (Tables 21 and 22). MM calculations show the energy profiles of benzaldehyde (40) and mesitaldehyde (41) to be rather similar in shape (curves A and B in Fig. 29). For both compounds, the coplanar state was found to be the initial state and the rotamers with the formyl group perpendicular to the ring plane were found to be the transition state. 2,4,6-Triethylbenzaldehyde (42) also has the same transition state conformation as compounds (40) and (41), according to the calculations, but the formyl and the three ethyl groups are on the opposite sides of the ring plane (curve C in Fig. 29). The minimum on the potential curve is found when the formyl group is 25° above the ring plane and all three ethyl groups are on the other side of the ring plane.

The barrier to internal formyl rotation estimated for 2,4,6-triisopropylbenzaldehyde (43) is only half of that found for 2,4,6-trineopentylbenzaldehyde (44) (Table 21). However, calculations show the opposite order (Table 22, curves D and E in Fig. 29). The order of barriers calculated may be a result of the "hard hydrogens" used in the MMP1 program. As shown earlier (page 100) the MMP1 program may give barriers that are too high for sterically strained systems, and molecule (43) is the more strained since it has six benzylic methyls while (44) only has three t-butyls. Unfortunately, the MMP2 program is only applicable to hydrocarbons and does not yet contain parameters for calculations on aromatic aldehydes.

The calculations show that the initial state conformation of compound (43) occurs when the formyl group is perpendicular to the ring plane and all isopropyl groups have their methine hydrogens in the ring plane. The methine hydrogens of the two ortho isopropyl groups are both facing the formyl group. Calculations (MMP1) made by Ito *et al.*¹⁸¹ on 2,4,6-triisopropylbenzophenone showed the same initial state, which is also in agreement with X-ray results on this compound in the solid state. Conformations in which one or none of the ortho methine hydrogens (still in the ring plane) faces the carbonyl group were calculated to be 7.9 and 9.6 kJmol^{-1} , respectively, higher in energy.

The transition state for compound (43) occurs when the formyl group is conjugated with the ring and the two ortho isopropyls are twisted so that their methine hydrogens are on opposite sides of the ring plane. One of the methine hydrogens is 20° above the ring plane while the other is 20° below the plane.

In the rotamer where only the methine proton in one of the two isopropyls is facing the carbonyl group (which is perpendicular to the ring plane) there are two possible modes for formyl rotation. One involves rotation so that the carbonyl oxygen passes a methine hydrogen, the other so that the oxygen passes two methyl groups in the other ortho isopropyl. Both modes of rotation give higher barriers (18.3 and 20.2 kJmol^{-1} , respectively) than found above.

For 2,4,6-trineopentylbenzaldehyde (44), MM calculations show initial state conformation to be when the formyl group is perpendicular to the ring plane, while the three neopentyl groups are on the opposite side, all perpendicular to the ring plane. The transition state conformation occurs when the formyl group lies in the ring plane, and all three neopentyl groups are on the same side of the plane as in the initial state.

Lunazzi *et al.*¹⁶⁵ have studied the rotational barrier of the formyl group in a series of ortho monoalkyl substituted benzaldehydes, where the ortho substituent was H, Me, Et, iPr or tBu. For the first four of these compounds, the rotational barrier was found to decrease from 32.2 to 27.1 to 26.9 to 24.7 kJmol^{-1} . This trend was explained by Lunazzi *et al.*¹⁶⁵ as follows: when the ortho substituent increases in size, the initial state deviates more and more from the planar conformation, while the transition state is unchanged, which makes the barriers decrease. The trend above, found by Lunazzi *et al.*, is in fairly good agreement with relaxation data (Table 21) on the aldehydes (40)-(43). The value of the barrier measured for 2,4,6-trineopentylbenzaldehyde (44) is very close to that of its triethylsubstituted analogue (42), and this seems reasonable since ^1H NMR measurements on the vinylic compounds (36) and (39) show that the barrier to internal rotation increases only moderately when the ortho ethyl groups are replaced by neopentyl groups.

IX.4 Discussion of systems with formimino groups

The restricted diffusion model was used to treat ^{13}C relaxation data on compounds (45)-(49) with the boundary condition $\theta = 90^\circ$ (Table 21). The trend in $\Delta G_{301}^\ddagger$ values for the formimino group rotation in the aldimines (45)-(49) is expected to be the same as that found for the corresponding aldehydes. However, the aldimines (47) and (48) show an order opposite to that found for the corre-

sponding aldehydes (42 and 43), but the difference in $\Delta G^\ddagger$ between (47) and (48) is very small. No MM calculations could be performed.

Ortho substituted benzaldimines have rarely been studied, except for a paper by Boyd *et al.*¹⁸², who studied the restricted $C_{sp^2}-C_{sp^2}(\text{aryl})$ bond rotation in two N-alkylbenzaldimines mono-substituted with a methyl and a phenyl group, respectively. Their results show that the barrier decreases as the size of the ortho substituent increases from methyl to the larger phenyl.

IX.5 Comparisons between systems

Results from the three different groups of compounds in chapters IX.2, IX.3 and IX.4 are most easily compared if two counteracting effects are considered, one due to steric effects and the other due to a delocalisation effect.

When an aromatic ring is substituted with a vinyl group (styrene) the delocalisation energy is very small. In styrene the steric effects (from the ortho hydrogens) partially outweigh that from delocalisation, and MM calculations show that the initial state is found when the vinyl group is twisted 30° out of the ring plane. If the substituent is a formyl group, as is the case for benzaldehyde, the delocalisation effect completely dominates the steric, as a result of the strong electronegative character of oxygen. The calculations therefore show the initial state for benzaldehyde when the carbonyl group lies in the ring plane.

When the ortho hydrogens in styrene are replaced by methyl and groups of larger size (compounds 35 and 37) the steric effects dominate, and according to the calculations the initial state in these cases occurs when the vinyl group is perpendicular to the ring plane. If the ortho hydrogens in benzaldehyde are replaced by methyl groups, the strong delocalisation effect still dominates, and the same initial state is found as for benzaldehyde. But when the ortho substituents are ethyl and groups of larger size, the calculations show that the steric effects outweigh the delocalisation effect. The calculations also show that the barrier to internal rotation in 2,4,6-triisopropylbenzaldehyde (43) is greater than that for 2,4,6-trineopentylbenzaldehyde (44). The relaxation time measurements show the opposite order, although the differences are small, and these results are in accordance with those of Lunazzi *et al.*^{165,180} on ortho mono-substituted benzaldehydes. The anomalous order calculated by the MMP1 program may be an effect from the "hard hydrogens" used in the program.

The effects of different ortho substituents in N-methylbenzaldimines will be very similar to those found for the corresponding aldehydes, since nitrogen is only slightly less electronegative than oxygen.

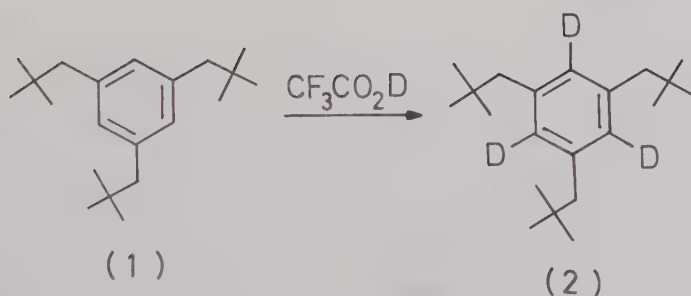
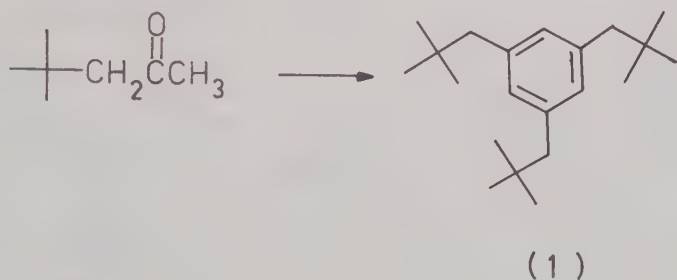
It is interesting to compare the above results for the benzaldehydes with those found when the formyl proton is replaced by a methyl group. In the case of acetophenone the initial state is found when the carbonyl group lies in the ring plane, due to dominance of the delocalisation effect.^{164,167} But when acetophenone is substituted with ortho methyl groups (acetylmesitylene) ¹H NMR chemical shifts and dipole measurements indicate that the acetyl group in the initial state is twisted 45° out of the ring plane, due to increased steric effects.¹⁶⁷ When the ortho substituents are neopentyl groups, Dahlberg *et al.*¹¹ found evidence for restricted internal rotation, and a barrier of 46 kJmol⁻¹ was estimated for 2-acetylTNB. The proposed initial state for 2-acetylTNB is a conformation with the carbonyl group perpendicular to the ring plane and on the side opposite to that of the three neopentyl groups (similar to that found for 2,4,6-trineopentylbenzaldehyde and 2,4,6-trineopentylstyrene). If the alpha methyl is replaced by a t-butyl group, Dahlberg *et al.*¹¹ estimated a barrier > 96 kJmol⁻¹ for 2-pivaloylTNB. When the substituents in TNB are vinyl or formyl groups, the barriers to internal rotation are very low (see page 100 for compound 37 and Tables 21 and 22 for compound 40). Nor does the introduction of a trans β-methyl group in compound (37) affect the low barrier (compound 38), but introduction of a cis β-methyl group leads to restricted internal rotation (similar to that observed by Dahlberg *et al.* in 2-alkyl and 2-acylTNB:s), and a barrier of 74 ± 2 kJmol⁻¹ could be estimated (see compound 39).

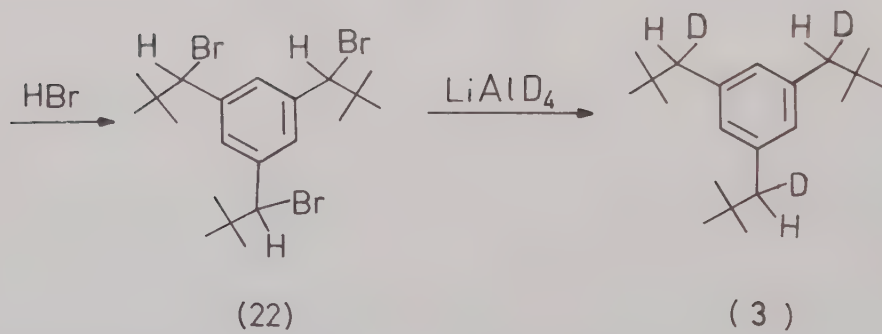
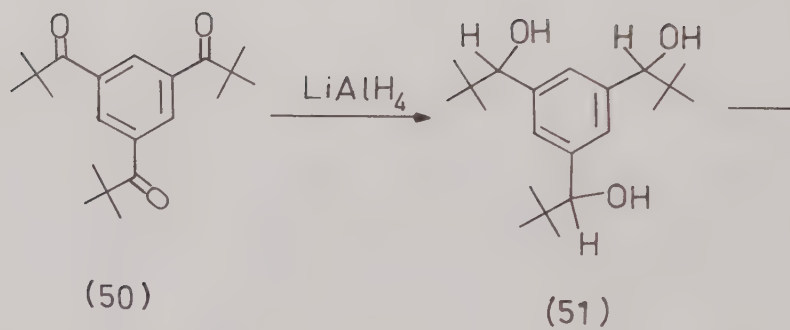
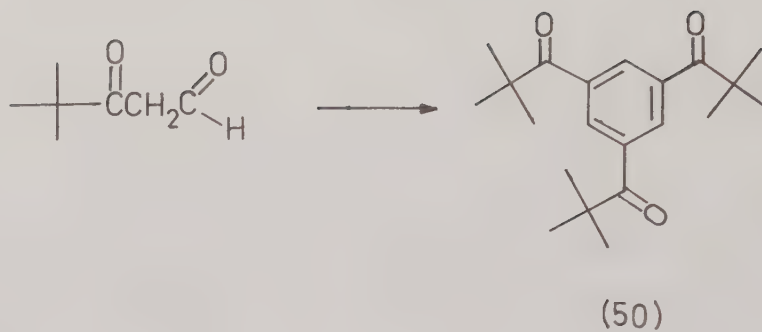
X. SYNTHETIC PART

X.1 Synthetic aspects of chapter V

1,3,5-Trineopentylbenzene (1) (TNB) was synthesised by cyclisation of methylneopentyl ketone, as described by Martinson and Marton.⁶

The specifically ring-deuterated compound 1,3,5-trineopentyl-2,4,6-tri-deuteriobenzene (2) was prepared from TNB and deuteriotrifluoroacetic acid as described by Olsson.⁴ Compound (3), 1,3,5-tris(1-deuterio-2,2-dimethylpropyl)benzene, was synthesised by lithium aluminium deuteride reduction of 1,3,5-tris(1-bromo-2,2-dimethylpropyl)benzene (22), which in turn was synthesised from the triol 1,3,5-tris(1-hydroxy-2,2-dimethylpropyl)benzene (51) by reaction with hydrogen bromide. The triol (51) was synthesised by Martinson⁵ by reduction of 1,3,5-tripivaloylbenzene (50) with hydrogen over palladium (5 %) on charcoal as catalyst, whereas I used lithium aluminium hydride for this reduction. 1,3,5-Tripivaloylbenzene was in turn synthesised from pivaloyl-acetaldehyde under Knoevenagel conditions, as described by Martinson.⁵





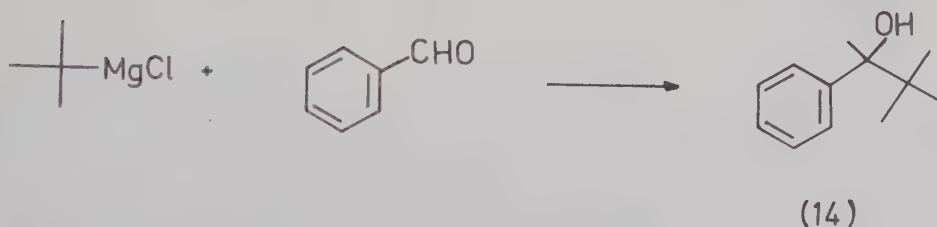
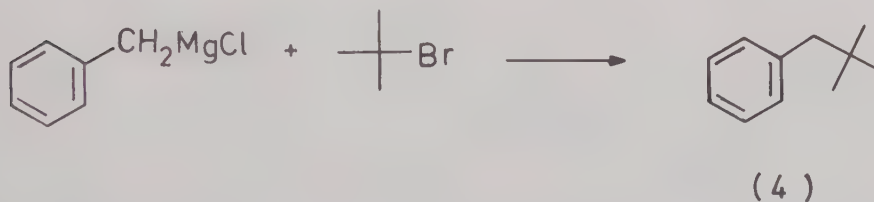
Scheme 1

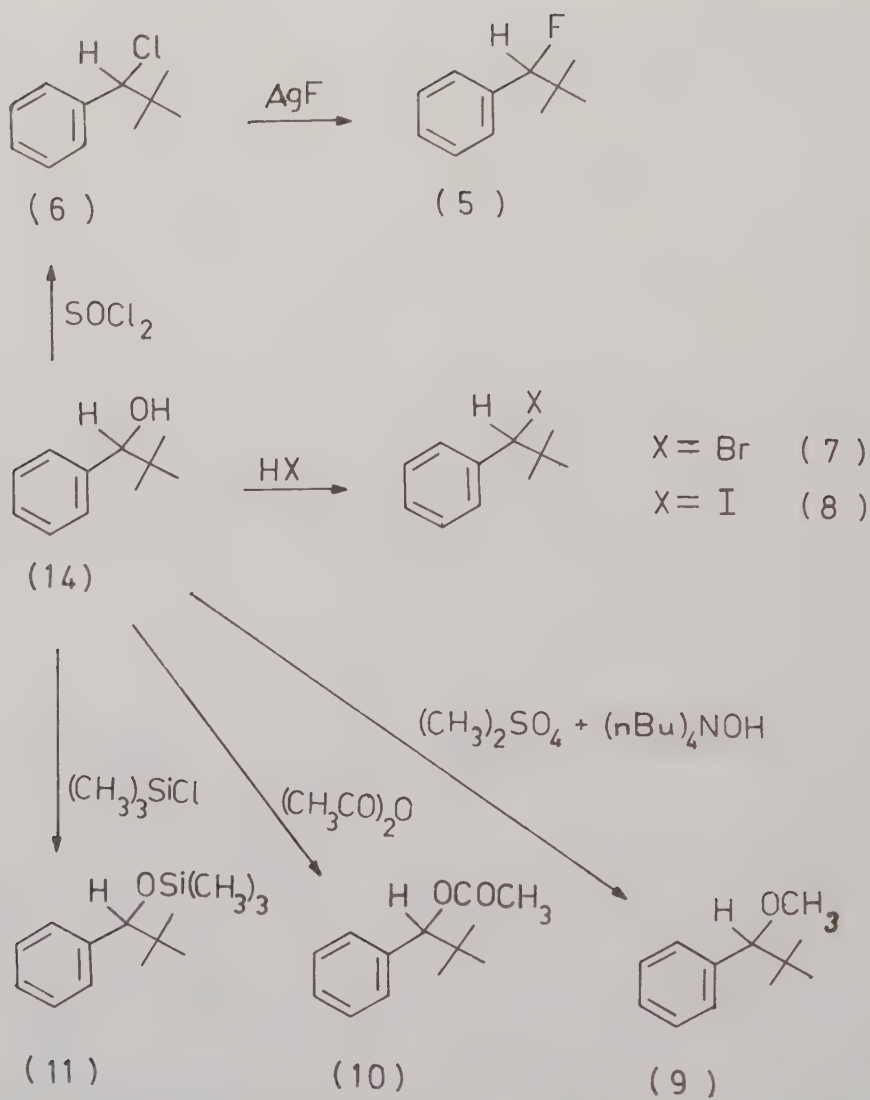
X.2 Synthetic aspects of chapter VI

Neopentylbenzene (4) was synthesised from benzyl magnesium chloride and t-butyl bromide according to Bygdén.¹⁸³

The alcohol 1-hydroxy-2,2-dimethylpropylbenzene (14)¹⁸⁴ was synthesised from benzaldehyde and t-butyl magnesium chloride, and was used as starting material for the syntheses of compounds (6)-(11) (see Scheme 2). Reaction between the alcohol (14) and appropriate reagents such as, thionyl chloride, hydrogen bromide and hydrogen iodide, afforded the compounds 1-chloro-2,2-dimethylpropylbenzene (6), 1-bromo-2,2-dimethylpropylbenzene (7) and 1-iodo-2,2-dimethylpropylbenzene (8), respectively. Reaction of compound (6) with silver fluoride in acetonitrile gave 1-fluoro-2,2-dimethylpropylbenzene (5).

The methyl ether 1-methoxy-2,2-dimethylpropylbenzene (9) was prepared from the alcohol (14) by reaction with dimethyl sulphate under conditions of phase transfer catalysis.¹⁸⁵ The compounds 1-acetoxy-2,2-dimethylpropylbenzene (10) and 1-trimethylsilyloxy-2,2-dimethylpropylbenzene (11) were prepared by reaction between the alcohol (14) and acetic anhydride in pyridine and trimethylsilyl chloride in pyridine, respectively.





Scheme 2

The alcohols 2-phenyl-3,3-dimethylbutane-2-ol (15), 3-phenyl-2,2-dimethylpentane-3-ol (16) and 3-phenyl-2,2-dimethylheptane-3-ol (17) were prepared by reaction between pivalophenone (phenyl-*t*-butyl ketone, 52) and the appropriate metal organic reagents: methyl magnesium iodide, ethyl lithium and *n*-butyl lithium, respectively (Scheme 3). The ketone pivalophenone (52) was in turn prepared by oxidation of the alcohol 1-hydroxy-2,2-dimethylpropylbenzene (14).^{186,187} Reaction between phenyl lithium and the ketones 2,2,4-trimethyl-3-pentanone (*t*-butyl-*i*-propyl ketone, 53)^{188,189} and 2,2,4,4-tetramethyl-3-pentanone (di-*t*-butyl ketone, 54)^{190,191} gave the alcohols 3-phenyl-2,2,4-trimethylpentane-3-ol (18) and 3-phenyl-2,2,4,4-tetramethylpentane-3-ol (19) respectively.

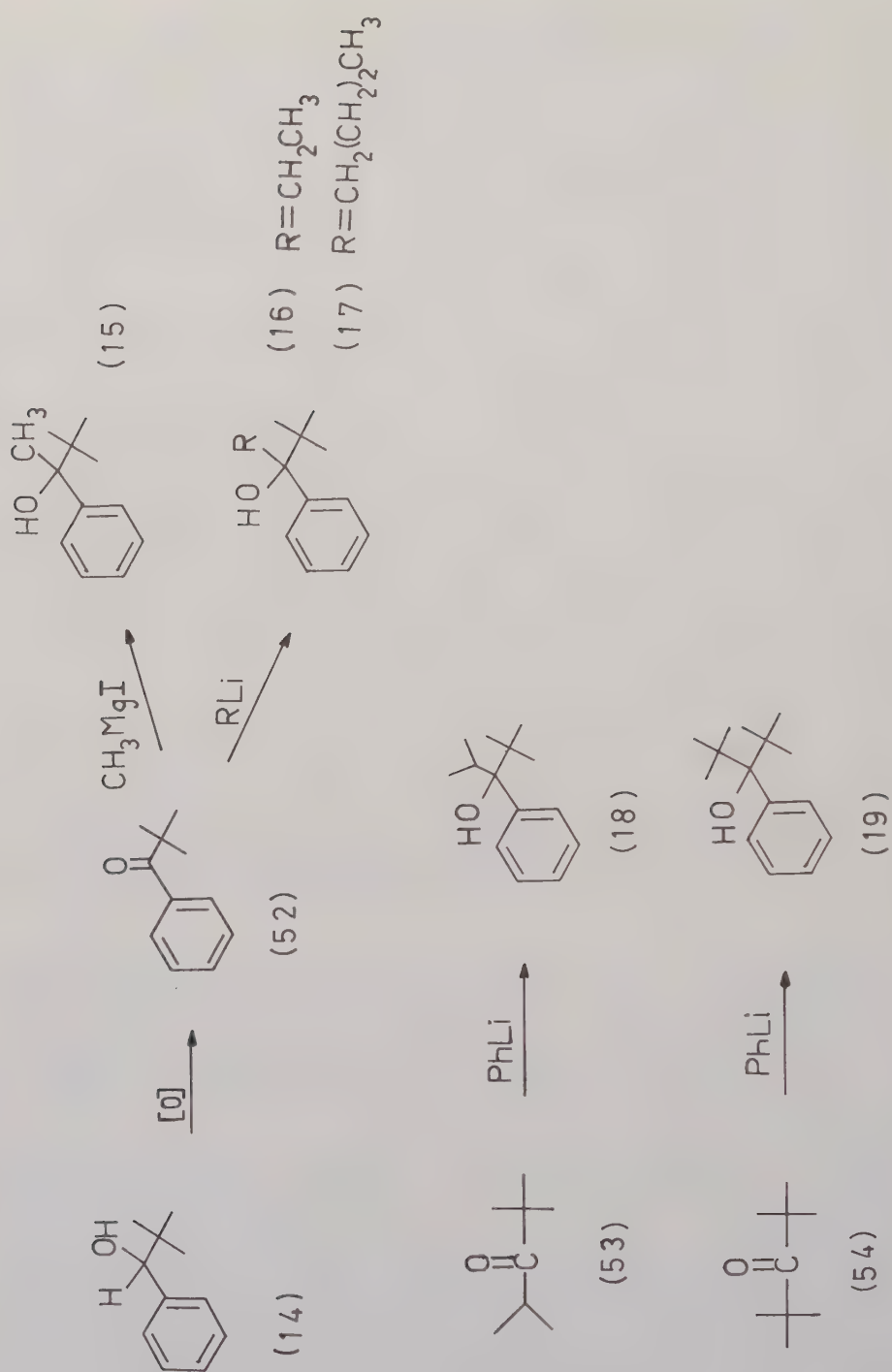
Compounds (12) and (13), 3-phenyl-2,2-dimethylbutane and 3-phenyl-2,2-dimethylpentane, respectively have been prepared¹⁹² by direct alkylation of the benzene ring with the secondary alcohols 2,2-dimethyl-3-butanol and 2,2-dimethyl-3-pentanol under Friedel Craft conditions. But according to Ramart-Lucas¹⁹³⁻¹⁹⁵, it should be possible to dehydrate the alcohols (15) and (16) by boiling with dilute acid, and only one olefinic product should be formed in each case. This method first seemed attractive because hydrogenation of the resulting olefins should then give the desired hydrocarbons (12) and (13).

However NMR and GC-MS analyses show that on boiling the alcohol (15) with dilute acid produces two isomeric olefins, α -*t*-butylstyrene (2-phenyl-3,3-dimethyl-1-butene (55); 52 %) and 3-phenyl-2,3-dimethyl-1-butene (56); (48 %). Other attempts to dehydrate with iodine still produced the two isomers in the same proportions (as above), and when phosphorous oxychloride in pyridine was used as the dehydrating agent the proportions of isomers (55) to (56) was 67 % to 33 %.

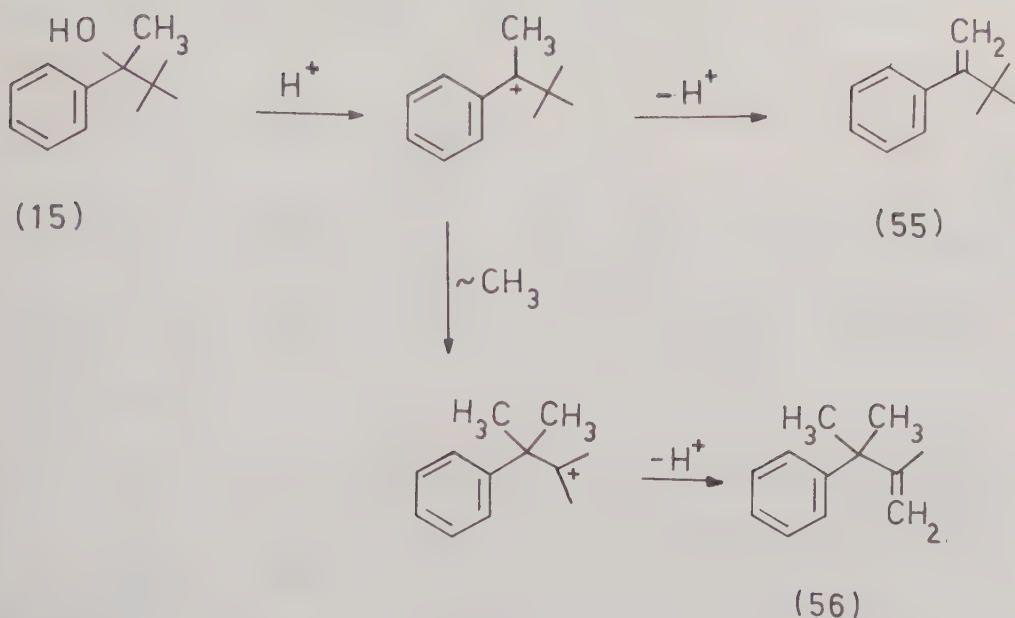
The production of the two isomers may be explained if one considers the first step in the dehydration reaction as the production of a carbonium ion. Then two paths are possible, elimination of a proton to give α -*t*-butylstyrene (55), and methyl group migration before proton elimination, which gives the butene (56) (Scheme 4).

Dehydration attempts (with iodine) on the alcohol (16) gave three products in proportions 1.9:1.0:1.1. The latter two were shown by NMR and GC-MS to be the *Z* and *E* isomers of 3-phenyl-4,4-dimethyl-2-pentene (57 and 58 in Scheme 5).

In the case of compound (18), dehydration attempts gave four products (separable by GC). One of the products, later identified as 3-phenyl-2,4,4-trimethyl-2-pentene (59) was formed in 82 % yield, while the three other compounds were not identified. No starting material was recovered.



Scheme 3



Scheme 4

Since the dehydration method produced olefin mixtures and further purification (by gas chromatography) seemed time consuming on a large scale, the olefins (55), (57+58) and (59) were prepared by reaction between pivalophenone (52) and appropriate triphenylalkylidene phosphoranes (Wittig reagents). Reaction between pivalophenone (52) and triphenylmethylene phosphorane¹⁹⁶ gave the olefin (55), which was reduced with hydrogen (Pd(10 %)) to 3-phenyl-2,2-dimethylbutane (12). When pivalophenone was reacted with triphenylethylidene phosphorane, the Z and E isomers of 3-phenyl-4,4-dimethyl-2-pentene (57+58) were formed (in a 9:11 ratio according to 1H NMR). No attempt was made to separate the isomers. The isomeric mixture of compounds (57) and (58) was instead hydrogenated (Pd(10 %)) to 3-phenyl-2,2-dimethylpentane (13). When pivalophenone was reacted with triphenylisopropylidene phosphorane¹⁹⁷ the olefin (59) was formed in low yield. However, compound (59) was not possible to hydrogenate (Pd(10 %)) to (60), probably due to steric hindrance preventing the double bond from coming into close proximity of the catalyst's surface.

Attempts to synthesise 3-phenyl-2,2,4,4-tetramethylpentane (61) from the alcohol (19) by Birch reduction,¹⁹⁸⁻²⁰¹ Lee's method^{202, 203} and reduction via tertiary chloride (unstable)²⁰⁴ all turned out to be unsuccessful.

X.3 Synthetic aspects of chapter VII

The triol 1,3,5-tris(1-hydroxy-2,2-dimethylpropyl)benzene (51) was the starting material for the syntheses of compounds (21), (22), (23), (25) and (26). Reaction between triol (51) and appropriate reagents as thionyl chloride, thionyl bromide (in HMPT), hydrogen iodide, acetic anhydride in pyridine and trimethylsilyl chloride in pyridine gave compounds (21), (22), (23), (25) and (26) (Scheme 6).

The synthesis of 1,3,5-tris(1-fluoro-2,2-dimethylpropyl)benzene (20) was achieved by reaction between compound (21) and silver fluoride in acetonitrile.

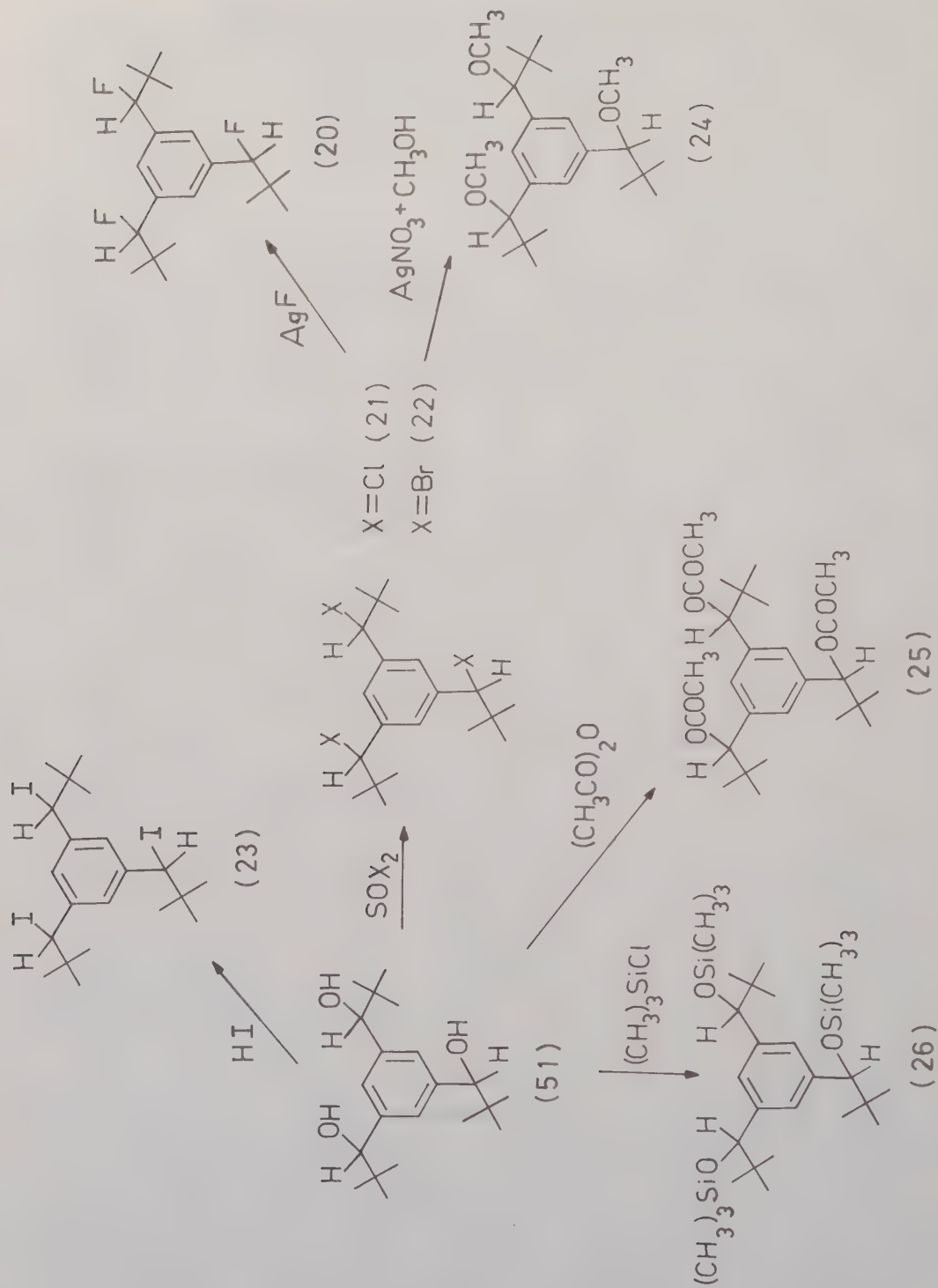
Attempts to prepare 1,3,5-tris(1-methoxy-2,2-dimethylpropyl)benzene (24) from the triol (51) by reaction with dimethyl sulphate under phase transfer catalysis conditions¹⁸⁵ were unsuccessful. Only one hydroxyl group was methylated (according to ¹H NMR) and then the reaction stopped. However if compound (22) was mixed with an equivalent amount of solid silver nitrate in boiling methanol 1,3,5-tris(1-methoxy-2,2-dimethylpropyl)benzene (24) was formed in nearly quantitative yield.

The precursor for the syntheses of compounds (27)-(33) was 1,3,5-tripivaloylbenzene (50). 1,3,5-Tris(1,1-dichloro-2,2-dimethylpropyl)benzene (29) and 1,3,5-tris(1,1-dibromo-2,2-dimethylpropyl)benzene (31) were prepared by reaction between 1,3,5-tripivaloylbenzene (50) and phosphorous pentachloride and phosphorous pentabromide, respectively (Scheme 7).

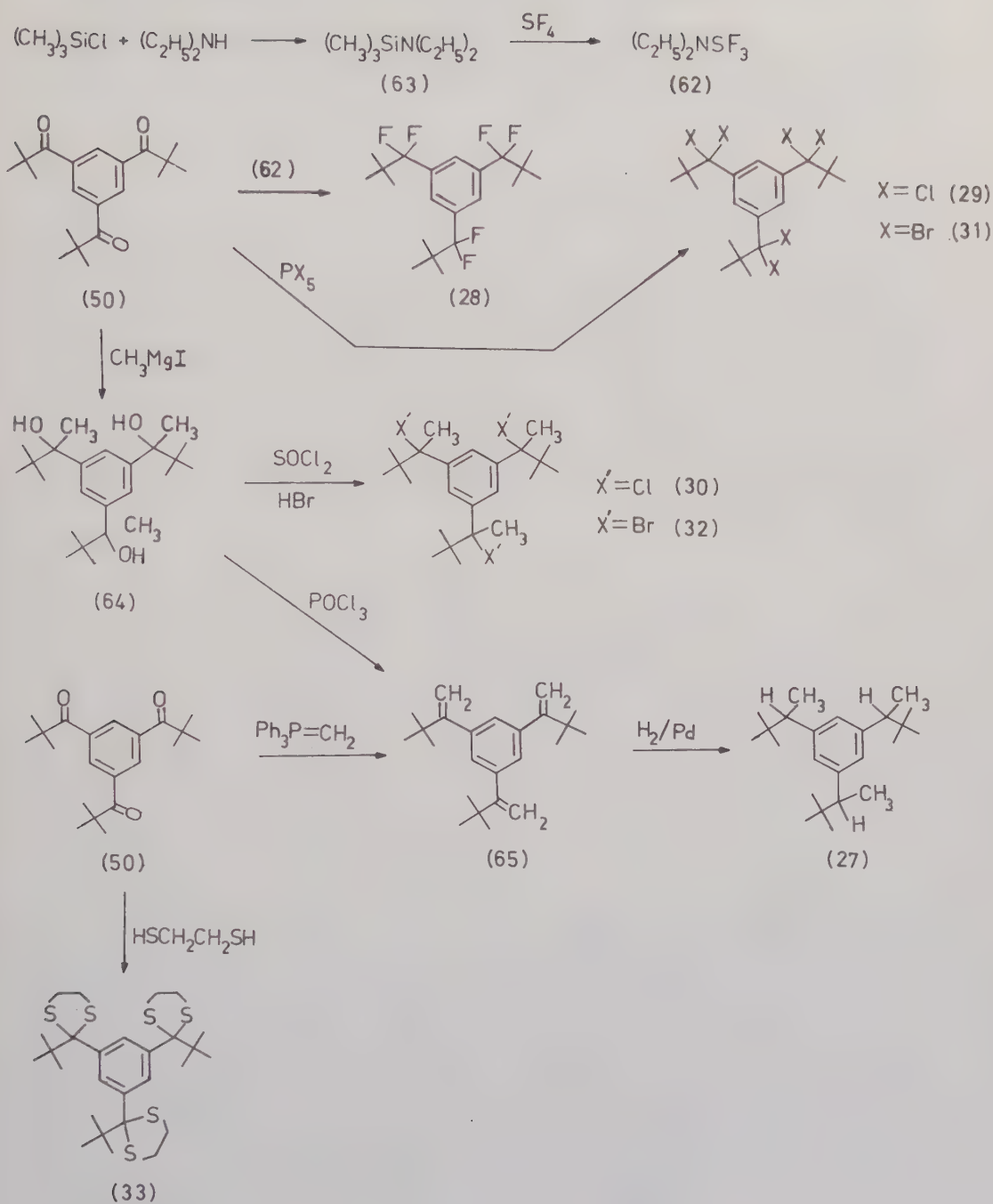
1,3,5-Tris(1,1-difluoro-2,2-dimethylpropyl)benzene (28) was prepared by reaction between 1,3,5-tripivaloylbenzene and the fluorinating agent diethylaminosulfur trifluoride (62).^{205,206} This fluorinating agent was prepared from sulfur tetrafluoride and diethyltrimethylsilylamine (63), which in turn was prepared from diethylamine and trimethylsilyl chloride.²⁰⁷

1,3,5-Tripivaloylbenzene trisethylenethioketal (33) was prepared from 1,3,5-tripivaloylbenzene and 1,2-ethanedithiol as described by Martinson.⁵

By treating 1,3,5-tripivaloylbenzene with methyl magnesium iodide, as described by Martinson,⁵ the triol 1,3,5-tris(1-hydroxy-1,2,2-trimethylpropyl)benzene (64) was prepared. Reaction between this triol and thionyl chloride or hydrogen bromide gave 1,3,5-tris(1-chloro-1,2,2-trimethylpropyl)benzene (30) and 1,3,5-tris(1-bromo-1,2,2-trimethylpropyl)benzene (32), respectively.



Scheme 6

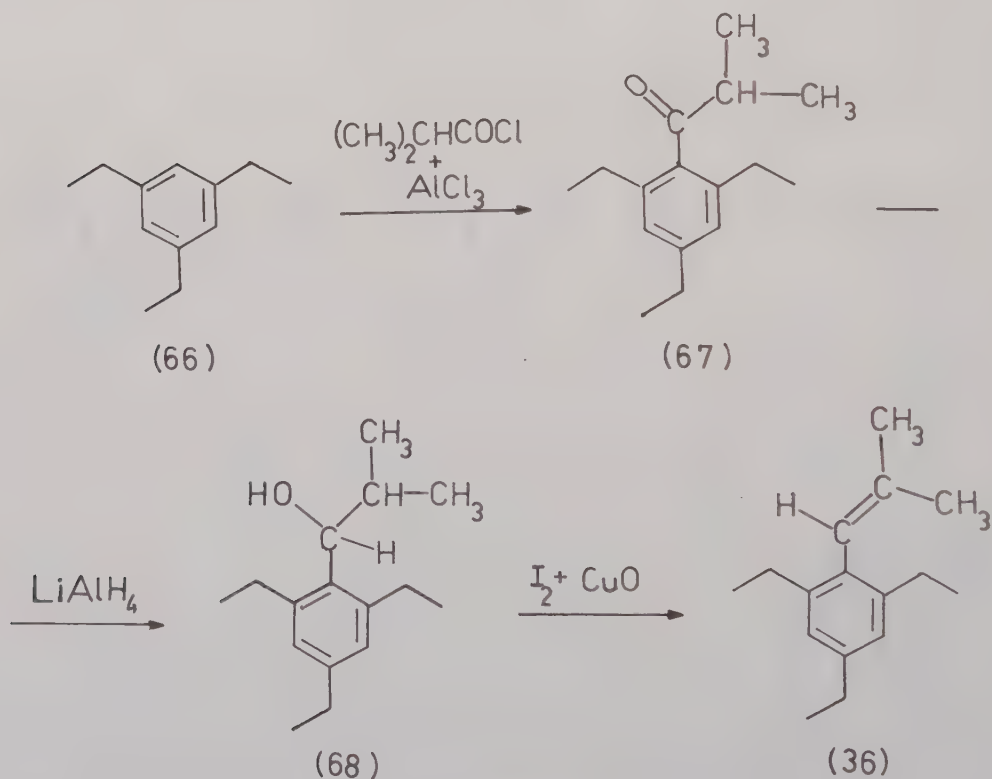


Scheme 7

Dehydration of (64) with phosphorous oxychloride gave the triolefin 1,3,5-tris(3,3-dimethylbutene-2-yl)benzene (65), which was hydrogenated (Pd (10 %)) to 1,3,5-tris(1,2,2-trimethylpropyl)benzene (27). The triolefin (65) could also be prepared by reaction between 1,3,5-tripivaloylbenzene (50) and the Wittig reagent triphenylmethylene phosphorane.¹⁹⁶

X.4 Synthetic aspects of chapter IX

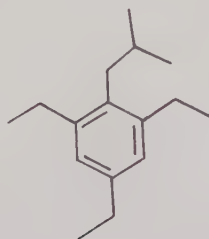
The syntheses of the vinylic compounds (35)-(39) all follow the same general pattern as shown in Scheme 8 for the synthesis of compound (36). The syntheses involve acylation of a 1,3,5-trialkyl substituted aryl compound with an appropriate acyl halide under Friedel Crafts conditions. The resulting 2-acyl-1,3,5-trialkylbenzene (cf. compound 67) was then reduced with lithium aluminium hydride to the corresponding 2(1-hydroxyalkyl)-1,3,5-trialkylbenzene (cf. compound 68), which in turn was dehydrated to the desired 2,4,6-trialkylstyrene (cf. compound 36).



Scheme 8

2,4,6-Trimethylstyrene (vinylmesitylene 35) was synthesised according to Klages *et al.*^{208,209} with the modification that phosphorous oxychloride in pyridine was used as dehydrating agent in the last step.²¹⁰

2(2,2-Dimethylvinyl)-1,3,5-triethylbenzene (36) was synthesised according to the Scheme 8 above. However the dehydration of compound (68) afforded some problems. First, it was attempted to dehydrate compound (68) by use of phosphorous oxychloride in pyridine (as in the synthesis of vinylmesitylene), but no reaction occurred. When iodine and red phosphorous (purified according to ref. 211) was used as reagent, which Dahlberg *et al.*¹¹ used in their synthesis of 2,4,6-trineopentylstyrene (37), two products were formed in the proportions 12:13 (according to GC). The first was identified as the desired product 2(2,2-dimethylvinyl)-1,3,5-triethylbenzene (36), and the second as 2(2-methylpropyl)-1,3,5-triethylbenzene (69) (shown by GC-MS and ¹H NMR).



(69)

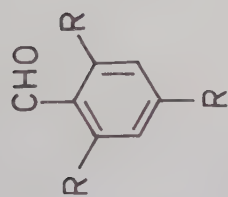
The production of compound (69) was realized as the result of the production of some hydrogen iodide during the reaction, which will reduce compound (68). The dehydration reaction was then carried out in the absence of red phosphorous, and the reaction product was found to consist to 89 % of compound (36) and to 11 % of compound (69). In order to completely avoid the production of hydrogen iodide in the reaction mixture a small amount of copper oxide was added. This completely suppressed the formation of compound (69) and produced only 2(2,2-dimethylvinyl)-1,3,5-triethylbenzene (36).

2,4,6-Trineopentylstyrene (37) was prepared as described by Dahlberg *et al.*¹¹ with the exception that the dehydration was performed with iodine and copper

oxide (described above) instead of with iodine and phosphorous as described by Dahlberg *et. al.*¹¹ The compounds 2(2-methylvinyl)-1,3,5-trineopentylbenzene (38) and 2(2,2-dimethylvinyl)-1,3,5-trineopentylbenzene (39) were synthesised by Dr. Dahlberg at the University of Gothenburg and were kindly supplied to me.

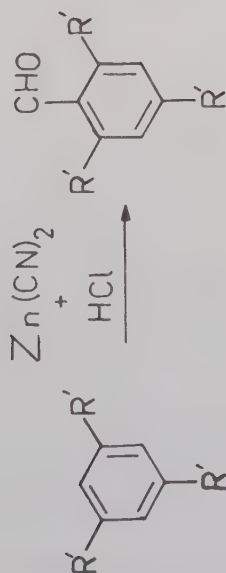
Benzaldehyde (40) and 2,4,6-trimethylbenzaldehyde (mesitaldehyde 41) were commercially available. 2,4,6-Triethylbenzaldehyde (42) was synthesised from 1,3,5-triethylbenzene via a Gattermann reaction involving reaction with zinc cyanide and hydrogen chloride.²¹⁹ 2,4,6-Triisopropylbenzaldehyde (43) and 2,4,6-trineopentylbenzaldehyde (44) were prepared from 1,3,5-triisopropylbenzene and 1,3,5-trineopentylbenzene, respectively, by reaction with dichloromethyl methylether and titanium tetrachloride,^{213,214} Scheme 9. Attempts to prepare 2,4,6-triisopropylbenzaldehyde (43) by the Gattermann method used above for compound (42) resulted in mixtures of isomeric aldehydes, due to the migration of the isopropyl groups during the reaction.

The N-methylaldimines (45)-(49) were synthesised by reaction between methyl amine and the corresponding aldehydes in an autoclave²¹⁵ Scheme 9.

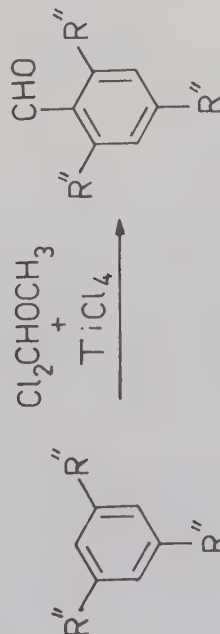


(40) $R=H$

(41) $R=CH_3$

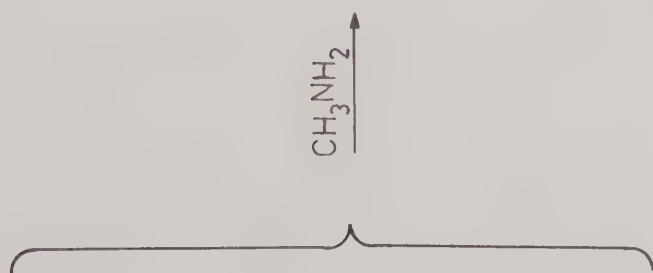


(42) $R'=CH_2CH_3$



(43) $R''=CH(CH_3)_2$

(44) $R''=CH_2C(CH_3)_3$



(45) $R'''=H$

(46) $R'''=CH_3$

(47) $R'''=CH_2CH_3$

(48) $R'''=CH(CH_3)_2$

(49) $R'''=CH_2C(CH_3)_3$

XI. EXPERIMENTAL

^1H NMR spectra for identifications were run on a JEOL JNM 60 spectrometer (unless otherwise stated), and in a few cases on a JEOL MH 100 spectrometer. The chemical shifts are reported in ppm downfield from tetramethylsilane. The multiplicities of the peaks are designated as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m).

The IR spectra were recorded on a Perkin Elmer 257 Grating Infrared spectrometer using cells of sodium chloride.

The mass spectra were determined on a LKB MS 9000 mass spectrometer operating with 70 eV electron energy and situated at the University of Lund. The high resolution mass spectra were obtained on a Varian MAT 311 mass spectrometer at the Department of Clinical Chemistry, University Hospital, Lund.

Melting points were obtained on a Kofler hot stage and are uncorrected.

Elementary analyses were performed by Analystjänst at the University of Lund.

The gas chromatographic (GLC) analyses in chapters V, VI and VII were carried out on a Varian 1400 Aerograph gas chromatograph. The column had 1/8 inch outer diameter and a length of 2 meter. The stationary phase was 3 % SE 30, silicon gum rubber on Chromosorb G, and the flow rate of nitrogen was 25 ml/min. In chapter IX the gas chromatographic analyses on compound (36) 2(2,2-dimethylvinyl)-1,3,5-triethylbenzene, and its precursors, were performed on the Varian 1400 Aerograph operating with temperature programming (4 °C/min.). The column used was a capillary column with OV-17 as the stationary phase, operating at a nitrogen flow rate of 5 ml/min.

XI.1 Preparative part

All chemicals were of reagent grade and were used without further purification, unless otherwise stated.

1,3,5-Trineopentylbenzene (1). M.p. 76-77 °C. (Lit. m.p. 76-77 °C).⁶

1,3,5-Trineopentyl-2,4,6-trideuteriobenzene (2). The product was pure according to gas chromatography⁴ and no aromatic protons could be detected by ^1H NMR spectroscopy, indicating more than 98 % deuterium in the aromatic ring.

1,3,5-Tripivaloylbenzene (50). M.p. 79-80 °C. (Lit. m.p. 79.5-80.5 °C).⁵

1,3,5-Tris(1-hydroxy-2,2-dimethylpropyl)benzene (51). 1,3,5-Tripivaloylbenzene (2.0 g, 6.7 mmol) dissolved in 15 ml of dry ether was added with cooling to a suspension of lithium aluminium hydride (6.9 g, 182 mmol) in 200 ml of dry ether. The mixture was refluxed and small samples were withdrawn, hydro-

lysed and studied by TLC (on alumina with cyclohexane as eluent). After 24 h, TLC showed a single product and the reaction mixture was then hydrolysed consecutively with 15 ml of ethyl acetate, 5 ml of 10 % solution of sodium hydroxide and 5 ml of water. The mixture was filtered and the filtrate evaporated to dryness leaving a white solid, which was recrystallised from ethanol-water (1:1) leaving 1.7 g, yield 65 %. The NMR spectrum was in accordance with that published by Martinson.⁵ M.p. 214-215 °C (Lit. 215 °C).⁵

1,3,5-Tris(1-bromo-2,2-dimethylpropyl)benzene (22). Compound (51) (0.73 g, 2.2 mmol) was dissolved in 50 ml of dry benzene. Dry gaseous hydrogen bromide (9.4 g, 116 mmol) was then added and the reaction mixture was stirred at room temperature. The reaction was followed by TLC (alumina with cyclohexane as eluent) and after 4 days only one product was detectable. The solvent was evaporated and the brown residue was decolourised by chromatography on a column of alumina with cyclohexane as eluent. After collection and evaporation of the solvent 1.1 g of a white crystalline compound remained, yield 92 %, m.p. 164-165 °C. (Found: C 48.3; H 6.13; Br 45.6. Calc. for $C_{21}H_{33}Br_3$: C 48.03; H 6.33; Br 45.64). 1H NMR (CCl_4): δ 1.03 (27H, s, $C(CH_3)_3$), 4.73 (3H, s, CHBr), 7.19-7.28 (3H, m, arom. H). IR (ν_{max} CCl_4): 2970 cm^{-1} (C-H str.), 1480 cm^{-1} (C=C str.). MS [m/e (%): 524 (2, M), 443 (14, $[M - ^{81}Br]$). Isotopic pattern in accordance with three bromines.

1,3,5-Tris(1-deuterio-2,2-dimethylpropyl)benzene (3). Compound (22) (0.32 g, 0.61 mmol) was dissolved in 10 ml of dry tetrahydrofuran and added dropwise to a suspension of lithium aluminium deuteride (1.0 g, 23.8 mmol) in 40 ml of dry tetrahydrofuran, with cooling. The mixture was then refluxed for 24 h and then hydrolysed consecutively with 5 ml of ethyl acetate, 5 ml of 10 % solution of sodium hydroxide and 5 ml of water and then filtered. The filtrate was evaporated, leaving an oily residue which was decolourised by chromatography on a column of alumina with hexane as eluent. Evaporation of the solvent left 0.16 g of a white crystalline compound, which was pure according to gas chromatography, m.p. 77-78 °C, yield 99 %. 1H NMR ($CDCl_3$): δ 0.91 (27H, s, $C(CH_3)_3$), 2.43 (3H, s, CHD) 6.68 (3H, s, arom. H). IR (ν_{max} , CCl_4): 1470 cm^{-1} (C=C str.). MS [m/e (%)] 291 (45, M).

Neopentylbenzene (4). B.p. 91-92 °C/38 torr, $n_D^{24} = 1.4882$. (Lit. b.p. 185.6-186.0 °C/757.6 torr, $n_D^{18} = 1.48837$).¹⁸³

1-Hydroxy-2,2-dimethylpropylbenzene (14). B.p. 97-98 °C/9 torr. (Lit. b.p. 95 °C/7 torr).¹⁸⁴

1-Chloro-2,2-dimethylpropylbenzene (6). Thionyl chloride (8.7 g, 73.2 mmol) was added to 1-hydroxy-2,2-dimethylpropylbenzene (4.0 g, 24.4 mmol) in a round bottomed flask. The reaction mixture was stirred for 4 h at room temperature

and was then poured into 30 ml of ice water. The aqueous phase was extracted 3 times with 10 ml of ether. The organic phases were collected, dried (MgSO_4), the ether evaporated and the residue distilled in vacuum to give 3.7 g of a colourless liquid, yield 82 %, b.p. $87-88^\circ\text{C}/6$ torr, $n_D^{25} = 1.5146$. (Lit. b.p. $89.5-90.5^\circ\text{C}/6.7$ torr, $n_D^{25} = 1.5142$). $^{216} \text{ }^1\text{H NMR (CDCl}_3\text{)}$: δ 1.04 (9H, s, $\text{C(CH}_3\text{)}_3$), 4.76 (1H, s, CH), 7.33 (5H, m, arom. H).

1-Fluoro-2,2-dimethylpropylbenzene (5). 1-Chloro-2,2-dimethylpropyl benzene (9.0 g, 49.4 mmol) was dissolved in 20 ml of dry acetonitrile. Anhydrous silver fluoride (9.4 g, 74.2 mmol) was added and the reaction mixture was refluxed for 10 h, with stirring. After cooling the reaction mixture was filtered, the solvent evaporated, 20 ml of water added and the aqueous phase extracted 3 times with 10 ml of cyclohexane. The organic phases were collected, dried (MgSO_4), the solvent evaporated and the residue distilled in vacuum giving 7.5 g of a colourless liquid, yield 91 %, b.p. $98-99^\circ\text{C}/28$ torr. (Found: C 81.2; H 6.84; F 11.9. Calc. for $\text{C}_{11}\text{H}_{15}\text{F}$: C 81.48; H 6.84; F 11.72). $^1\text{H NMR (CDCl}_3\text{)}$: 0.93 (9H, s, $\text{C(CH}_3\text{)}_3$), 5.06 (1H, d, CHF, $J_{\text{HF}} = 46$ Hz), 7.30 (5H, s, arom. H). IR (ν_{max} CCl_4): 1455 cm^{-1} (C=C str.), 1040 cm^{-1} (C-H def.). MS [m/e (%): 166 (4, M), 147 (4, [M-F]).

1-Bromo-2,2-dimethylpropylbenzene (7). Dry hydrogen bromide (5.9 g, 73.2 mmol) was absorbed in a three necked flask containing 1-hydroxy-2,2-dimethylpropylbenzene (4.0 g, 24.4 mmol) according to the method of Norris *et al.*.²¹⁷ After 12 h, the reaction mixture was worked up.²¹⁷ The product was distilled in vacuum to give 2.8 g of a colourless liquid, yield 50 %, b.p. $96-98^\circ\text{C}/6$ torr, $n_D^{21} = 1.5389$. (Lit. b.p. $109^\circ\text{C}/10$ torr, $n_D^{20} = 1.5398$, b.p. $114-115^\circ\text{C}/15$ torr, b.p. $103-104^\circ\text{C}/7.5$ torr). $^{217-221} \text{ }^1\text{H NMR (CDCl}_3\text{)}$: δ 1.05 (9H, s, $\text{C(CH}_3\text{)}_3$), 4.82 (1H, s, CH), 7.33 (5H, m, arom. H).

1-Iodo-2,2-dimethylpropylbenzene (8). Dry hydrogen iodide (9.4 g, 73.4 mmol), made by reaction between 66 % ($\rho = 1.94\text{ g/ml}$) hydroiodic acid with an excess of phosphorous pentoxide plus a catalytic amount of red phosphorous, was absorbed into a three necked flask containing 1-hydroxy-2,2-dimethylpropylbenzene (4.0 g, 24.4 mmol), as described by Norris *et al.*²¹⁷ After 12 h of reaction time, followed by work up, the product was distilled in vacuum to give 4.0 g of a colourless liquid, yield 60 %, b.p. $104-105^\circ\text{C}/8$ torr, (Found: C 48.4; H 5.62; I 45.9. Calc. for $\text{C}_{11}\text{H}_{15}\text{I}$: C 48.35; H 5.50; I 46.15). $^1\text{H NMR (CDCl}_3\text{)}$: δ 1.06 (9H, s, $\text{C(CH}_3\text{)}_3$), 5.03 (1H, s, CH), 7.33 (5H, m, arom. H). IR (ν_{max} CCl_4): 3035 cm^{-1} (=C-H str.), 1180 cm^{-1} (C-H def.). MS [m/e (%): 259 (2, [M-CH₃]), 147 (3, [M-I]).

1-Methoxy-2,2-dimethylpropylbenzene (9). This substance was prepared from 1-hydroxy-2,2-dimethylpropylbenzene (4.0 g, 24.4 mmol), dimethyl sulphate

(4.4 g; 34.9 mmol) and sodium hydroxide (5.2 ml, 50 %), by the phase transfer catalysis method described by Merz.¹⁸⁵ Tetra-n-butyl ammonium hydrogen sulphate (0.05 g) was the transfer catalyst. The reaction time was 3½ h, and was not optimized. After work up, the reaction product was chromatographed on a column of alumina with cyclohexane as eluent. After collection, the eluent was evaporated, and the residue distilled in vacuum to give 2.0 g of a colourless liquid, yield 45 %, b.p. 77-78 °C/8 torr. (Lit. 94-95 °C/20 torr).²²² (Found: C 80.4; H 10.2. Calc. for C₁₂H₁₈O: C 80.8; H 10.1). ¹H NMR (CDCl₃): δ 0.86 (9H, s, C(CH₃)₃), 3.20 (3H, s, OCH₃), 7.33 (5H, s, arom. H).

1-Acetoxy-2,2-dimethylpropylbenzene (10). This substance was synthesised from 1-hydroxy-2,2-dimethylpropylbenzene (1.0 g, 6.1 mmol), acetic anhydride (3.8 g, 37.0 mmol) and dry pyridine (5 ml) according to the general method described by Hauser *et al.*²²³ After work up, the residue was distilled in vacuum to give 0.91 g of a colourless liquid, yield 73 %, b.p. 103-104 °C/6 torr. (Lit. b.p. 123-124 °C/16 torr).²²² (Found: C 75.3; H 8.60. Calc. for C₁₃H₁₈O₂: C 75.70; H 8.73). ¹H NMR (CDCl₃): δ 0.97 (9H, s, C(CH₃)₃), 2.14 (3H, s, COCH₃), 5.60 (1H, s, CH), 7.40 (5H, s, arom. H).

1-Trimethylsilyloxy-2,2-dimethylpropylbenzene (11). This compound was synthesised from 1-hydroxy-2,2-dimethylpropylbenzene (0.5 g, 3.1 mmol), trimethyl chlorosilane (0.5 g, 4.6 mmol) and dry pyridine (10 ml) according to the general method described by Birkhofer *et al.*²²⁴ After work up, the reaction product was distilled in vacuum to give 0.65 g of a colourless liquid, yield 92 %, b.p. 88-89 °C/6 torr. (Found: C 70.9; H 9.84; Si 12.3. Calc. for C₁₄H₂₄OSi: C 71.10; H 10.17; Si 11.90). ¹H NMR (CDCl₃): δ 0 (9H, s, Si(CH₃)₃), 0.95 (9H, s, C(CH₃)₃), 4.30 (1H, s, CH), 7.33 (5H, s, arom. H). IR (ν_{max} CCl₄): 3014 cm⁻¹ (=C-H str.), 1100 cm⁻¹ (C-O-Si str.). MS [m/e (%): 236 (1, M), 179 (100, [M-tBu]).

Phenyl-t-butyl ketone (pivalophenone) (52). The methods published by Hampton *et al.*¹⁸⁶ and Neidrig *et al.*¹⁸⁷ were followed, b.p. 120-121 °C/23 torr, n_D²¹ = 1.5077. (Lit. b.p. 110-111 °C/18 torr, 103-104 °C/13 torr, n_D^{19,2} = 1.5086).^{186,187}

2-Phenyl-3,3-dimethylbutane-2-ol (15). This substance was prepared from phenyl-t-butyl ketone (16.4 g, 0.10 mol) and methyl magnesium iodide (0.21 mol) according to Ramart-Lucas.²²⁵ B.p. 120-121 °C/19 torr, n_D²² = 1.5127. (Lit. b.p. 116-117 °C/15 torr, n_D²⁵ = 1.5135).²²⁵

3-Phenyl-2,2-dimethylpentane-3-ol (16). Ethyllithium (0.23 mol) in dry ether (prepared according to ref. 226) was added dropwise to phenyl-t-butyl ketone (17.2 g, 0.11 mol) in a three necked flask. The reaction mixture was refluxed for 12 h. then hydrolysed with 50 ml of a saturated solution of ammonium chloride and extracted with 3 x 15 ml of ether. The organic phases were col-

lected, dried (MgSO_4) and the ether evaporated. The residue was distilled in vacuum, to give 15.4 g of a colourless liquid, yield 75 %, b.p. 97-98 °C/4 torr, $n_D^{25} = 1.509$. (Lit. b.p. 115-116 °C/11 torr, $n_D^{25} = 1.5064$, b.p. 118-120 °C/15 torr, $n_D^{25} = 1.5105$).^{227,228}

3-Phenyl-2,2-dimethylheptane-3-ol (17). This substance was prepared from phenyl-*t*-butyl ketone (3.0 g, 18.5 mmol) and *n*-butyllithium (12.4 ml, 1.49 M) in hexane according to the procedure described above for 3-phenyl-2,2-dimethylpentane-3-ol. The reaction time was 24 h. After work up there was 3.4 g of a colourless liquid, yield 83 %, b.p. 108-109 °C/4 torr. (Found: C 81.8; H 10.81. Calc. for $\text{C}_{15}\text{H}_{24}\text{O}$: C 81.81; H 10.90). ^1H NMR (CDCl_3): δ 0.90 (9H, s, $\text{C}(\text{CH}_3)_3$), 0.85-1.40 (7H, m, CH_2 and CH_3), 1.80 (1H, s, OH), 1.70-2.10 (2H, t, CH_2), 7.14-7.66 (5H, s, arom. H). IR (ν_{max} CCl_4): 3610 cm^{-1} (O-H str.). MS [m/e (%): 202 (14, $[\text{M}-\text{H}_2\text{O}]$), 183 (100, $[\text{M}-\text{H}_2\text{O}-\text{Et}]$), 163 (17, $[\text{M}-\text{tBu}]$).

2,4,4-Trimethyl-3-pentanone (isopropyl-*t*-butyl ketone; 53). This ketone was prepared by oxidation of 3-hydroxy-2,2,4-trimethylpentane (prepared by reaction between *i*-butyraldehyde and *t*-butylmagnesium chloride) as described by Favorski and Fritzman,^{188,189} b.p. 134-135 °C. (Lit. b.p. 134-135 °C).¹⁸⁹

3-Phenyl-2,4,4-trimethylpentane-3-ol (18). Isopropyl-*t*-butyl ketone (5.0 g, 39.1 mmol) was added dropwise to a solution of phenyllithium²²² (19.6 ml, 2 M) in 70 % benzene and 30 % ether, under nitrogen atmosphere. The reaction mixture was stirred for 12 h at room temperature, then hydrolysed with 50 ml of water and worked up as described for 3-phenyl-2,2-dimethylpentane-3-ol (16). After distillation there was 4.0 g of a colourless liquid, yield 49 %, b.p. 93-94 °C/1-2 torr. (Found: C 81.2; H 10.60. Calc. for $\text{C}_{14}\text{H}_{22}\text{O}$: C 81.55; H 10.68). ^1H NMR (CDCl_3): δ 0.71 (3H, d, CH_3 , $J = 7$ Hz), 0.96 (9H, s, $\text{C}(\text{CH}_3)_3$), 1.10 (3H, d, CH_3 , $J = 7$ Hz), 1.68 (1H, s, OH), 2.58 (1H, m, CH, $J = 7$ Hz), 7.10-7.80 (5H, m, arom. H). IR (ν_{max} CCl_4): 3620 cm^{-1} (O-H str.). MS [m/e (%): 206 (1, M), 163 (18, $[\text{M}-\text{iPr}]$), 149 (100, $[\text{M}-\text{tBu}]$).

2,2,4,4-Tetramethyl-3-pentanone (di-*t*-butyl ketone; 54). This ketone was prepared from pivaloyl chloride and *t*-butylmagnesium chloride as described in refs. 190,191, b.p. 152-153 °C, $n_D^{22} = 1.4187$. (Lit. b.p. 152-153 °C, b.p. 69.5 °C/48 torr, $n_D^{20} = 1.4192$, $n_D^{25} = 1.4170$).^{190,191}

3-Phenyl-2,2,4,4-tetramethylpentane-3-ol (19). This compound was synthesised from di-*t*-butyl ketone and phenyllithium (prepared according to ref. 226) by the procedure of Bartlett *et al.*¹³⁵ b.p. 140-142 °C/11 torr, $n_D^{25} = 1.5232$. (Lit. b.p. 140-143 °C/12 torr, 148-151 °C/15 torr, $n_D^{25} = 1.5230$).¹³⁵

2-Phenyl-3,3-dimethylbutene (α -*t*-butylstyrene; 55). Triphenylmethylene phosphorane was synthesised from triphenyl-methyl phosphonium bromide (16.0 g, 44.7 mmol) and *n*-butyllithium (30 ml, 1.49 M), as described in ref. 189.

Phenyl-t-butyl ketone (6.0 g, 44.7 mmol) dissolved in 50 ml of dry ether was added and the reaction mixture was refluxed for 20 h. The mixture was then hydrolysed with 50 ml of water, the phases separated and the aqueous phase extracted with two 40 ml portions of ether. The organic phases were collected, dried (MgSO_4) and the solvent evaporated, leaving a liquid residue, which was chromatographed on a column of alumina with hexane as eluent. Two fractions were collected (with R_f -values 0.72 and 0.33). The solvent was evaporated from the first fraction, leaving 4.4 g of a colourless liquid, yield 73 %, b.p. 91-92 °C/15 torr, $n_D^{22} = 1.5013$. (Lit. b.p. 88-92 °C/15 torr).^{193,194} ^1H NMR (CDCl_3): δ 1.11 (9H, s, $\text{C}(\text{CH}_3)_3$), 4.81 (1H, d, CH_2 , $J = 1\text{ Hz}$), 5.20 (1H, d, CH_2 , $J = 1\text{ Hz}$), 7.25 (5H, s, arom. H). Evaporation of the solvent from the second fraction, and NMR analysis showed the residue to be unreacted start material.

Mixture of Z and E 3-phenyl-4,4-dimethyl-2-pentene (57 + 58). Triphenyl-ethylidene phosphorane was synthesised from triphenylethyl phosphonium bromide (5.53 g, 14.9 mmol) and n-butyllithium (10 ml, 1.49 M) in hexane. Phenyl-t-butyl ketone (2.0 g, 14.9 mmol) dissolved in 25 ml of dry ether was added and the procedure described above for 2-phenyl-3,3-dimethylbutene was followed. After work up there was 2.2 g of a colourless liquid, yield 85 %, b.p. 92-93 °C/12 torr, $n_D^{22} = 1.5140$. (Lit. b.p. 91-93 °C/12 torr, $n_D^{25} = 1.5155$).¹⁹⁵ ^1H NMR (CDCl_3): δ 1.33 (s, $\text{C}(\text{CH}_3)_3$), 1.85 (d, CH_3 , $J = 8\text{ Hz}$), 5.24 (q, CH, $J = 8\text{ Hz}$), 6.80-7.40 (m, arom. H+ CH, $J_{\text{CH}} = 8\text{ Hz}$ partly overlapping). A mixture of two isomers with the methyl group cis and trans to the phenyl group.

2-Methyl-3-phenyl-4,4-dimethyl-2-pentene (59). Triphenylisopropylidene phosphorane was prepared, according to the general procedure described above, from triphenylisopropyl phosphonium iodide (13.0 g, 29.8 mmol, prepared according to ref. 190) and n-butyllithium (20 ml, 1.49 M). Phenyl-t-butyl ketone (4.0 g, 24.7 mmol) was added according to the above procedure. After refluxing for 72 h and work up, there remained 0.37 g of an oily colourless liquid, yield 7 %. (Found: C 89.4; H 10.6. Calc. for $\text{C}_{14}\text{H}_{20}$: C 89.36; H 10.64). ^1H NMR (CDCl_3): δ 0.95 (12H, s+s, $\text{CH}_3 + \text{C}(\text{CH}_3)_3$), 1.08 (3H, s, CH_3), 7.06-7.59 (5H, m, arom. H). IR (ν_{max} CCl_4): 3010 cm^{-1} (=C-H str.). MS [m/e (%): 188 (17, M), 173 (100, $[\text{M}-\text{CH}_3]$), 131 (72, $[\text{M}-\text{tBu}]$).

3-Phenyl-2,2-dimethylbutane (12). 2-Phenyl-3,3-dimethylbutene (2.5 g, 15.6 mmol) was dissolved in 75 ml of absolute ethanol. Palladium (10 % on charcoal, 0.4 g) was added and the mixture was hydrogenated in a Parr apparatus at a hydrogen pressure of 490 kPa. When the theoretical amount of hydrogen had been absorbed the reaction mixture was filtered, the ethanol evaporated and the residue chromatographed on a column of alumina with hexane as eluent. Evaporation of the solvent left 1.7 g of a clear liquid, yield 70 %, b.p. 77-78 °C/8

torr, $n_D^{21} = 1.4951$. (Lit. b.p. 205-207 °C, $n_D^{25} = 1.4942$). $^{192} \text{ }^1\text{H}$ NMR (CDCl_3): δ 0.86 (9H, s, $\text{C}(\text{CH}_3)_3$), 1.24 (3H, d, CH_3 , $J = 7$ Hz), 2.57 (1H, q, CH, $J = 7$ Hz), 7.21 (5H, s, arom. H).

3-Phenyl-2,2-dimethylpentane (13). A mixture of Z and E 3-phenyl-4,4-dimethyl-2-pentene (1.0 g, 5.8 mmol) was hydrogenated and worked up as described for 3-phenyl-2,2-dimethylbutane above. After work up 0.64 g of a colourless liquid remained, yield 64 %, b.p. 93-94 °C/8 torr, $n_D^{21} = 1.4921$. (Lit. b.p. 221-223 °C, $n_D^{25} = 1.4912$). $^{192} \text{ }^1\text{H}$ NMR (CDCl_3): δ 0.66 (3H, t, CH_3 , $J = 7$ Hz), 0.87 (9H, s, $\text{C}(\text{CH}_3)_3$), 1.33-2.40 (3H, m, CH and CH_2 , $J_{\text{CH}_2} = 7$ Hz), 7.19 (5H, s, arom. H).

1,3,5-Tris(1-chloro-2,2-dimethylpropyl)benzene (21). Thionyl chloride (6.4 g, 53.7 mmol) was added to 1,3,5-tris(1-hydroxy-2,2-dimethylpropyl)benzene (2.0 g, 6.0 mmol) with cooling. The reaction mixture was then heated to 60 °C with stirring. Small samples were taken, hydrolysed and analysed by TLC (on alumina with cyclohexane as eluent). After 12 h the reaction was found to be complete, and the reaction mixture was hydrolysed with 20 ml of water and extracted with three 15 ml portions of ether. The organic phases were collected, dried (MgSO_4) and the solvent evaporated, leaving a brown residue, which was chromatographed on a column of alumina with cyclohexane as eluent. Collection and evaporation of the solvent left 2.2 g of a white crystalline residue, yield 99 %, m.p. 158-159 °C. (Found: C 64.7; H 8.53; Cl 26.8. Calc. for $\text{C}_{21}\text{H}_{33}\text{Cl}_3$: C 64.37; H 8.43; Cl 27.20). ^1H NMR (CDCl_3): δ 1.03 (27H, s, $\text{C}(\text{CH}_3)_3$), 4.72 (3H, s, CHCl), 7.26 (3H, m, arom. H). IR (ν_{max} CCl_4): 1480 cm^{-1} (C=C str.). MS [m/e (%): 390 (2, $\text{M}^{(35}\text{Cl})$), 355 (3, $[\text{M}-^{35}\text{Cl}]$), 333 (3, $[\text{M}-\text{tBu}]$) isotopic pattern in agreement with 3 chlorines.

1,3,5-Tris(1-fluoro-2,2-dimethylpropyl)benzene (20). 1,3,5-Tris(1-chloro-2,2-dimethylpropyl)benzene (3.0 g, 7.6 mmol) was dissolved in 40 ml of dry acetonitrile. Silver fluoride (5.8 g, 46.0 mmol) was added and the mixture was refluxed for 36 h. After this time a ^1H NMR spectrum showed complete reaction. The reaction mixture was filtered, the acetonitrile evaporated, 20 ml of water added and the aqueous phase extracted with three 15 ml portions of ether. The ether was evaporated and a yellow residue was left, which was chromatographed on a column of silica with a mixture of cyclohexane: methylene chloride (2:1) as eluent. Collection and evaporation of the solvent left 2.2 g of a white product which crystallised after a few days, yield 86 %, m.p. 85-86 °C. (Found: C 73.7; H 9.42; F 16.8. Calc. for $\text{C}_{21}\text{H}_{33}\text{F}_3$: C 73.71; H 9.65; F 16.69). ^1H NMR (CDCl_3): δ 0.96 (27H, s, $\text{C}(\text{CH}_3)_3$), 5.14 (3H, d, CHF , $J_{\text{HF}} = 46$ Hz), 7.10-7.25 (3H, m, arom. H). IR (ν_{max} CCl_4): 1465 cm^{-1} (C=C str.). MS [m/e (%): 342 (3, M), 285 (7, $[\text{M}-\text{tBu}]$).

1,3,5-Tris(1-bromo-2,2-dimethylpropyl)benzene (22). 1,3,5-Tris(1-hydroxy-

2,2-dimethylpropyl)benzene (3.2 g, 9.5 mmol) was dissolved in 25 ml of dry HMPT. Thionyl bromide (23.5 g, 113.0 mmol) was added and the mixture was stirred at room temperature. Small samples were taken and analysed by ^1H NMR. After 5 days the reaction was found to be complete. The reaction mixture was poured into 65 ml of water and the aqueous phase was extracted with eight 25 ml portions of hexane. The organic extracts were combined dried (MgSO_4) and the solvent evaporated leaving a brown residue, which was chromatographed on a column of alumina with cyclohexane as eluent. Collection and evaporation left 2.6 g of a white crystalline residue, yield 51 %, m.p. 164-165 $^\circ\text{C}$. (Lit. m.p. 164-165 $^\circ\text{C}$).²²⁹

^1H NMR, IR and MS spectra are in accordance with those published.

1,3,5-Tris(1-iodo-2,2-dimethylpropyl)benzene (23). Dry hydrogen iodide (8.6 g, 67.2 mmol), made from reaction between 66 % ($\rho = 1.94 \text{ gml}^{-1}$) hydroiodic acid and an excess of phosphorous pentoxide plus a catalytic amount of red phosphorous (0.1 g), was condensed into a three necked flask containing 1,3,5-tris(1-hydroxy-2,2-dimethylpropyl)benzene (2.5 g, 7.4 mmol) at -60 $^\circ\text{C}$. The reaction mixture was stirred at this temperature for 10 h, after which time TLC (on alumina with cyclohexane as eluent) showed complete reaction. The reaction mixture was allowed to reach room temperature, 15 ml of water was added to the semisolid residue and the aqueous phase was extracted three times with 20 ml of benzene. Collection of the organic extracts, drying (MgSO_4) and evaporation of the solvent left a red solid residue which was chromatographed on a column of alumina with hexane as eluent. Collection and evaporation of the solvent left 3.3 g of a white crystalline residue, yield 67 %, m.p. 168-169 $^\circ\text{C}$. (Found: C 38.3; H 5.06; I 56.7. Calc. for $\text{C}_{21}\text{H}_{33}\text{I}_3$: C 37.84; H 4.95; I 57.21). ^1H NMR (CDCl_3): δ 1.06 (27H, s, $\text{C}(\text{CH}_3)_3$), 4.97 (3H, s, CHI), 7.14-7.20 (3H, m, arom. H). IR (ν_{max} CCl_4): 1485 cm^{-1} (C=C str.). MS [m/e (%): 609 (2, [M-tBu]), 539 (100, [M-I])].

1,3,5-Tris(1-methoxy-2,2-dimethylpropyl)benzene (24). 1,3,5-Tris(1-bromo-2,2-dimethylpropyl)benzene (0.83 g, 1.6 mmol) was mixed with solid silver nitrate (2.0 g, 11.9 mmol) and 40 ml of dry methanol. The reaction mixture was refluxed for 12 h until TLC (on alumina, methylene chloride as eluent) showed the reaction to be complete. The mixture was filtered, the methanol evaporated and the semisolid yellow residue chromatographed on a column of alumina. The column was first eluted with hexane to eliminate some impurities, then with methylene chloride to eluate the product. After collection and evaporation of the solvent there remained 0.5 g of a white crystalline residue, yield 76 %, m.p. 72-73 $^\circ\text{C}$. (Found: C 76.2; H 10.9. Calc. for $\text{C}_{24}\text{H}_{42}\text{O}_3$: C 76.12; H 11.19). ^1H NMR (CDCl_3): δ 0.91 (27H, s, $\text{C}(\text{CH}_3)_3$), 3.15 (9H, s, OCH_3), 3.85 (3H, s, CH), 6.86-7.11 (3H, s, arom. H). IR (ν_{max} CCl_4): 1100 cm^{-1} (C-O-C str.). MS [m/e (%):

378 (1, M), 363 (6, [M-CH₃]), 321 (100, [M-tBu]).

1,3,5-Tris(1-acetoxy-2,2-dimethylpropyl)benzene (25). 1,3,5-Tris(1-hydroxy-2,2-dimethylpropyl)benzene (1.0 g, 3.0 mmol) was dissolved in 15 ml of dry pyridine and acetic anhydride (9.0 g, 15 mmol) was added. The reaction mixture was stirred at room temperature, and the reaction was followed by ¹H NMR. After 4 days NMR showed the reaction to be complete, and 30 ml of water was added to the reaction mixture. The aqueous phase was extracted twice with 10 ml of ethyl acetate. The organic phases were collected and washed three times with 10 ml of a 10 % solution of sodium hydrogen carbonate, 10 ml of water, dried (MgSO₄) and the ethyl acetate evaporated leaving a solid residue, which was chromatographed on a column of alumina with ethyl acetate as eluent. Collection and evaporation of the ethyl acetate left 1.1 g of a white crystalline residue, yield 81 %, m.p. 118-119 °C. (Found: C 70.3; H 9.21; Calc. for C₂₇H₄₂O₆: C 70.13; H 9.09). ¹H NMR (CDCl₃): δ 0.92 (27H, s, C(CH₃)₃), 2.09 (9H, s, COCH₃), 5.54 (3H, s, CH), 7.16 (3H, s, arom. H). IR (ν_{max} CC1₄): 1730 cm⁻¹ (C=O str.). MS [m/e (%): 462 (1, M), 405 (2, [M-tBu]), 346 (13, [M-tBu-OAc]).

1,3,5-Tris(1-trimethylsilyloxy-2,2-dimethylpropyl)benzene (26). 1,3,5-Tris(1-hydroxy-2,2-dimethylpropyl)benzene (0.5 g, 1.5 mmol) was dissolved in 10 ml of dry pyridine, trimethyl chlorosilane (0.98 g, 9.0 mmol) was added, and the mixture was refluxed. After 24 h of refluxing ¹H NMR showed the reaction to be complete, and 50 ml of water was added. The aqueous phase was extracted twice with 15 ml of ether and the organic phases were collected. After washing three times with 15 ml of water, the organic phase was dried (MgSO₄) and the solvent evaporated. The residue was chromatographed on a column of alumina with cyclohexane as eluent. Collection and evaporation of the solvent left 0.75 g of a white crystalline product, yield 91 %, m.p. 138-139 °C. (Found: C 65.7; H 11.0; Si 14.8. Calc. for C₃₀H₆₀O₃Si₃: C 65.18; H 10.86; Si 15.26). ¹H NMR (CDCl₃): δ 0 (27H, s, Si(CH₃)₃), 0.94 (27H, s, C(CH₃)₃), 4.34 (3H, s, CH), 7.10-7.21 (3H, m, arom. H). IR (ν_{max} KBr): 1245 cm⁻¹ (Si-C def.). MS [m/e (%): 552 (1, M), 537 (4, [M-CH₃]), 495 (100, [M-tBu]).

Diethyl-trimethylsilylamine (63). B.p. 126-127 °C/760 torr, n_D²³ = 1.4104. (Lit. b.p. 126.8-127.1 °C/738 torr, b.p. 126.1-126.4 °C/760 torr, n_D²⁰ = 1.4112).²⁰⁷

Diethylaminosulfur trifluoride (62) B.p. 43-44 °C/12 torr. (Lit. b.p. 43-44 °C/12 torr).^{205,206}

1,3,5-Tris(1,1-difluoro-2,2-dimethylpropyl)benzene (28). 1,3,5-Tripivaloylbenzene (2.0 g, 6.1 mmol) dissolved in 15 ml of dry carbon tetrachloride was added slowly to diethylaminosulfur trifluoride (3.4 g, 21.1 mmol) in a three necked flask with external cooling. The reaction mixture was then heated to reflux. After refluxing for 40 min., the reaction mixture was cooled, and poured

into 30 g of ice-water. The organic layer was separated, and the aqueous phase extracted with three 15 ml portions of carbon tetrachloride. The organic phases were collected, the solvent evaporated, leaving a tan-coloured crystalline residue. The residue was chromatographed on a column of silica (deactivated with 10 % of water) with cyclohexane as eluent. Collection and evaporation of the solvent left 2.3 g of a white crystalline product, yield 98 %, m.p. 112-113 °C. High resolution mass spectrometry gave MW = 396.2252 u. The value for $C_{21}H_{30}F_6$ is 396.2252 u. 1H NMR ($CDCl_3$): δ 1.04 (27H, s, $C(CH_3)_3$), 7.49 (3H, s, arom. H). IR (ν_{max} CCl_4): 1080 cm^{-1} (C-F str.). MS [m/e (%): 396 (5, M), 381 (23, [M-CH₃]), 339 (31, [M-tBu]).

1,3,5-Tris(1,1-dichloro-2,2-dimethylpropyl)benzene (29). 1,3,5-Tripivaloylbenzene (2.0 g, 6.1 mmol) was mixed with phosphorous pentachloride (4.8 g, 23.0 mmol) and heated to 115 °C with stirring. Small samples were taken, hydrolysed and analysed by TLC (on silica gel, with cyclohexane as developer). After 10 h reaction time at 115 °C, the reaction was found to be complete (TLC), and the mixture was cooled, hydrolysed with 25 ml of water and extracted with four 15 ml portions of benzene. The organic phases were collected and the solvent was evaporated, leaving a brown residue. The residue was chromatographed on a column of silica (deactivated by 10 % of water), with cyclohexane as eluent. Collection and evaporation of the solvent left 2.4 g of a white crystalline product, yield 82 %, m.p. 196-197 °C. (Found: C 50.7; H 6.00; Cl 42.9; Calc. for $C_{21}H_{30}Cl_6$: C 50.91; H 6.06; Cl 43.03). 1H NMR ($CDCl_3$): δ 1.20 (27H, s, $C(CH_3)_3$), 8.16 (3H, s, arom. H). IR (ν_{max} CCl_4): 1475 cm^{-1} (C=C str.). MS [m/e (%): 493 (1, M($5^{35}Cl + 3^{37}Cl$)), 459 (5, M($4^{35}Cl + 2^{37}Cl$)- ^{37}Cl). Isotopic pattern in agreement with 6 chlorines.

1,3,5-Tris(1,1-dibromo-2,2-dimethylpropyl)benzene (31). 1,3,5-Tripivaloylbenzene (2.0 g, 6.1 mmol) was mixed with phosphorous pentabromide (8.9 g, 20.7 mmol) and the mixture was heated to 80 °C and stirred. Small samples were taken from time to time, hydrolysed and analysed by TLC (on silica gel, with methylene chloride as developer). After 5 days the reaction was found to be complete (TLC showed only one spot), and the mixture was cooled, hydrolysed with 35 ml of water and extracted with six 20 ml portions of hot benzene. The organic layers were combined and the solvent evaporated. A greyish crystalline residue was left, which was recrystallised from large volumes of hot ethyl acetate. After three recrystallisations there remained 1.9 g of a white crystalline product, yield 40 %, m.p. 262-263 °C. (Found: C 32.5; H 4.00; Br 62.5. Calc. for $C_{21}H_{30}Br_6$: C 33.07; H 4.04; Br 62.99). 1H NMR ($CDCl_3$): δ 1.28 (27H, s, $C(CH_3)_3$), 8.40 (3H, s, arom. H). IR (ν_{max} CCl_4): 1490 cm^{-1} (C=C str.). MS [m/e (%): 747 (1, M($3^{79}Br + 3^{81}Br$)-CH₃), 705 (1, M($3^{79}Br + 3^{81}Br$)-tBu). Isotopic pattern in

accord with 6 bromines.

1,3,5-Tripivaloylbenzene trisethylenethioketal (33). M.p. 266-267 °C. (Lit. m.p. 266-267 °C).⁵

1,3,5-Tris(1-hydroxy-1,2,2-trimethylpropyl)benzene (64). M.p. 139-140 °C. (Lit. m.p. 139-140 °C).⁵

1,3,5-Tris(1-chloro-1,2,2-trimethylpropyl)benzene (30). Thionyl chloride (4.2 g, 35.5 mmol) was added with cooling to 1,3,5-tris(1-hydroxy-1,2,2-trimethylpropyl)benzene (1.5 g, 4.0 mmol) in a three necked flask. The reaction mixture was stirred and heated to 60 °C. Small samples were taken, hydrolysed and analysed by TLC (on silica gel, with cyclohexane as developer). After 24 h the reaction was found to be complete and the reaction mixture was cooled, hydrolysed with 20 ml of water and extracted with three 10 portions of ether. Collection of the organic phases, drying (Na_2SO_4) and evaporation of the solvent left a brown residue, which was chromatographed on a column of silica (deactivated with 15 % of water) with cyclohexane as eluent. Collection and evaporation of the solvent left 1.6 g of a white crystalline residue, yield 93 %, m.p. 187-188 °C. (Found: C 66.8; H 9.21; Cl 24.2. Calc. for $\text{C}_{24}\text{H}_{39}\text{Cl}_3$: C 66.44; H 9.00; Cl 24.56). ^1H NMR (CDCl_3): δ 1.03 (27H, s, $\text{C}(\text{CH}_3)_3$), 2.10 (9H, s, CH_3), 7.67 (3H, m, arom. H). IR (ν_{max} CCl_4): 1605 cm^{-1} (C=C str.). MS [m/e (%): 419 (4, $\text{M}(2^{35}\text{Cl} + ^{37}\text{Cl})-\text{CH}_3$), 417 (4, $\text{M}(^{35}\text{Cl})-\text{CH}_3$), 375 (18, $\text{M}(3^{35}\text{Cl})-\text{tBu}$). Isotopic pattern corresponds to three chlorines.

1,3,5-Tris(1-bromo-1,2,2-trimethylpropyl)benzene (32). Dry hydrogen bromide (0.35 g, 4.3 mmol) was absorbed in a solution of 1,3,5-tris(1-hydroxy-1,2,2-trimethylpropyl)benzene (0.27 g, 0.7 mmol) dissolved in 15 ml of dry benzene. The reaction mixture was stirred at room temperature. The reaction was followed by ^1H NMR, and after 9 h the reaction was found to be complete. Stirring was maintained for additional 4 h and then the solvent was evaporated, leaving a brown crystalline residue, which was recrystallised from hot diisopropyl ether. After three recrystallisations there remained 0.24 g of a white crystalline product, yield 60 %, m.p. 188-189 °C. (Found: C 51.0; H 7.00; Br 41.9. Calc. for $\text{C}_{24}\text{H}_{39}\text{Br}_3$: C 50.79; H 6.88; Br 42.32). ^1H NMR (CDCl_3): δ 1.08 (27H, s, $\text{C}(\text{CH}_3)_3$), 2.29 (9H, s, CH_3), 7.63-7.85 (3H, m, arom. H). IR (ν_{max} CCl_4): 1485 cm^{-1} (C=C str.). MS [m/e (%): 551 (2, $\text{M}(2^{79}\text{Br} + ^{81}\text{Br})-\text{CH}_3$), 509 (3, $\text{M}(2^{79}\text{Br} + ^{81}\text{Br})-\text{tBu}$). Isotopic pattern corresponds to three bromines.

1,3,5-Tris(3,3-dimethylbutene-2-yl)benzene (65). Phosphorous oxychloride (0.73 g, 4.8 mmol) was added to 1,3,5-tris(1-hydroxy-1,2,2-trimethylpropyl)benzene (0.5 g, 1.3 mmol) dissolved in 6 ml of dry pyridine, with external cooling. The reaction mixture was then refluxed for 24 h until ^1H NMR showed complete reaction. The 30 ml of water was added and the aqueous phase was

extracted with two 15 ml portions of cyclohexane. Collection of the organic phases, drying (MgSO_4) and evaporation of the solvent left a yellow viscous product which was chromatographed on a column of alumina with cyclohexane as eluent. Collection and evaporation of the solvent left 0.41 g of an oily colourless product, yield 96 %. (Found: C 88.4; H 10.9. Calc. for $\text{C}_{24}\text{H}_{36}$: C 88.89; H 11.11). ^1H NMR (CDCl_3): δ 1.13 (27H, s, $\text{C}(\text{CH}_3)_3$), 4.79 (3H, d, CH, $J_{\text{HHgem}} = 2.5$ Hz), 5.16 (3H, d, CH, $J_{\text{HHgem}} = 2.5$ Hz), 6.79 (3H, s, arom. H). IR (ν_{max} CCl_4): 3090 cm^{-1} (C-H str.). MS [m/e (%): 324 (47, M), 309 (57, $[\text{M}-\text{CH}_3]$). Substance (65) could also be synthesised by adding a solution of 1,3,5-tripival-oylbenzen (1.0 g, 3.0 mmol) in 10 ml of dry ether to a solution of triphenyl-methylene phosphine (9.1 mmol), prepared according to ref. 189, in dry ether. Dimethyl sulfoxide (10 ml) was then added and the mixture was refluxed for 24 h. After hydrolysis with 25 ml of water, the aqueous phase was extracted with several 10 ml portions of cyclohexane. Work up and decolourisation as described above gave an identical product (0.92 g), yield 93 %.

1,3,5-Tris(1,2,2-trimethylpropyl)benzene (27). 1,3,5-Tris(3,3-dimethylbutene-2-yl)benzene (1.0 g, 3.1 mmol) was dissolved in 50 ml of absolute ethanol, 10 % Pd on charcoal (0.15 g) was added and the mixture was hydrogenated in a Parr apparatus at a hydrogen pressure of 490 kPa. When the theoretical amount of hydrogen had been absorbed, the reaction mixture was filtered by use of celite, the solvent evaporated and the residue chromatographed on a column of alumina with hexane as eluent. Collection and evaporation of the solvent left 1.0 g of a white crystalline product, yield 98 %, m.p. $84-85^\circ\text{C}$. (Found: C 87.3; H 12.7. Calc. for $\text{C}_{24}\text{H}_{39}$: C 87.27; H 12.73). ^1H NMR (CDCl_3): δ 0.85 (27H, s, $\text{C}(\text{CH}_3)_3$), 1.25 (9H, d, CH_3 , $J = 7$ Hz), 2.53 (3H, q, CH, $J = 7$ Hz), 6.80 (3H, s, arom. H). IR (ν_{max} CCl_4): 1600 cm^{-1} (C=C str.). MS [m/e (%): 330 (9, M), 315 (7, $[\text{M}-\text{CH}_3]$), 273 (100, $[\text{M}-\text{tBu}]$).

1,3,5-Triethylbenzene (66). This substance was synthesised and purified according to refs. 230, 233; b.p. $103-104^\circ\text{C}/19$ torr, $n_{\text{D}}^{20} = 1.4972$. (Lit. b.p. $216^\circ\text{C}/760$ torr, $n_{\text{D}}^{20} = 1.4969$). ²³⁰⁻²³³

2(2-Methylpropanoyl)-1,3,5-triethylbenzene (63). Aluminium chloride (33.9 g, 0.25 mol) was covered with 100 ml of dry carbon disulphide in a three necked flask. Isobutyryl chloride (28.6 g, 0.25 mol) was added with cooling and the mixture was stirred for 15 min. 1,3,5-Triethylbenzene (25.6 g, 0.16 mol) dissolved in 40 ml of dry carbon disulphide was added slowly, with cooling. The temperature was then allowed to rise and the reaction mixture was stirred at ca. 40°C . Small samples were taken, hydrolysed and analysed by GLC. After 2 h GLC showed the reaction to be complete (99 % had reacted). The reaction mixture was hydrolysed with 50 ml of water, the carbon disulphide evaporated

and the aqueous phase extracted with five 30 ml portions of hexane. The organic phases were collected, washed with 15 ml of 10 % solution of sodium chloride, 15 ml of water, dried (MgSO_4) and the solvent evaporated. An oily colourless residue was left, which was chromatographed on a column of silica with methylene chloride as eluent. Evaporation of the solvent left 29.9 g of an colourless oil, which was pure according to GLC, yield 82 %. (Found: C 82.6; H 10.4. Calc. for $\text{C}_{16}\text{H}_{24}\text{O}$: C 82.69; H 10.42). ^1H NMR (100 MHz CDCl_3): δ 1.09 (3H, d, CH_3), 1.15 (3H, t, CH_3 , $J = 11$ Hz), 1.17 (6H, t, CH_3 , $J = 11$ Hz), 1.38 (3H, d, $J = 7$ Hz), 2.56 (4H, q, CH_2 , $J = 11$ Hz), 2.58 (2H, q, CH_2 : $J = 11$ Hz), 2.91 (1H, m, CH, $J = 7$ Hz). 6.83 (2H, s, arom. H). IR (ν_{max} CCl_4): 1700 cm^{-1} (C=O str.). MS [m/e (%): 232 (3, M), 189 (100, [M-iPr]), 161 (3, [M-CO-iPr]).

2(1-Hydroxy-2-methylpropyl)-1,3,5-triethylbenzene (68). Lithium aluminium hydride (19.6 g, 0.52 mol) was covered with 100 ml of dry ether in a three necked flask. 2(2-Methylpropanoyl)-1,3,5-triethylbenzene (19.8 g, 0.11 mol) dissolved in 50 ml of dry ether was added dropwise with cooling and stirring. The mixture was then refluxed and small samples were taken hydrolysed and analysed by GLC. After 15 h GLC showed the reaction to be complete (99 % had reacted). The reaction mixture was cooled, hydrolysed consecutively with 20 ml of ethyl acetate, 20 ml of water and 10 ml of a 10 % solution of sodium hydroxide. The organic and the aqueous phases were separated and the aqueous phase was extracted with 15 ml of cyclohexane. The organic phases were collected, dried (MgSO_4) and the solvent evaporated leaving a light yellow viscous residue, which was chromatographed on a column of silica with methylene chloride as eluent. Evaporation of the solvent left 18.0 g of a colourless liquid, which was pure according to GLC, yield 91 %. (Found: C 81.8; H 10.9. Calc. for $\text{C}_{16}\text{H}_{26}\text{O}$: C 81.98; H 11.19). ^1H NMR (100 MHz CDCl_3): δ 0.64 (3H, d, CH_3 , $J = 7$ Hz), 1.12 (3H, d, CH_3 , $J = 7$ Hz), 1.17 (6H, t, CH_3 , $J = 11$ Hz), 1.26 (3H, t, CH_3 , $J = 11$ Hz), 1.79 (1H, s, OH), 1.9-2.4 (1H, m, CH), 2.61 (2H, q, CH_2 , $J = 11$ Hz), 2.73 (4H, q, CH_2 , $J = 11$ Hz), 4.56 (1H, d, CH, $J = 11$ Hz), 6.75 (2H, s, arom. H). IR (ν_{max} CCl_4): 3495 cm^{-1} (OH str.), 1390 cm^{-1} (C-O str.). MS [m/e (%): 234 (6, M), 191 (100, [M-iPr]), 161 (7, [M-iPr-CHOH]).

Reaction of 2(1-hydroxy-2-methylpropyl)-1,3,5-triethylbenzene with iodine and red phosphorous. 2(1-Hydroxy-2-methylpropyl)-1,3,5-triethylbenzene (3.0 g, 12.8 mmol) was mixed with purified 211 red phosphorous (10.7 g, 86.2 mmol) in 70 ml of cyclohexane. Iodine (10.7 g, 42.2 mmol) dissolved in 200 ml of cyclohexane was added, and the reaction mixture was refluxed. The reaction was followed by GLC, and after 20 h the reaction was complete. Two products were formed in the ratio 52:48. They were identified (GC-MS and NMR) as 2(2,2-di-

methylvinyl)-1,3,5-triethylbenzene and 2(2-methylpropyl)-1,3,5-triethylbenzene.

Reaction of 2(1-hydroxy-2-methylpropyl)-1,3,5-triethylbenzene with iodine. 2(1-Hydroxy-2-methylpropyl)-1,3,5-triethylbenzene (0.1 g, 0.4 mmol) was dissolved in 10 ml of cyclohexane. Iodine (0.5 g, 2.0 mmol) dissolved in 70 ml of cyclohexane was added and the same procedure as above was followed. After 20 h GLC showed the reaction to be complete and the reaction mixture now consisted to 89 % of 2(2,2-dimethylvinyl)-1,3,5-triethylbenzene and to 11 % of 2(2-methylpropyl)-1,3,5-triethylbenzene.

2(2,2-Dimethylvinyl)-1,3,5-triethylbenzene (36). Reaction of 2(1-hydroxy-2-methylpropyl)-1,3,5-triethylbenzene with iodine and copper oxide. 2(1-Hydroxy-2-methylpropyl)-1,3,5-triethylbenzene (1.0 g, 4.0 mmol) was mixed with copper oxide (0.05 g) in 10 ml of cyclohexane. Iodine (4.0 g, 15.9 mmol) dissolved in 500 ml of cyclohexane was added and the above procedure was followed. After 20 h, GLC showed the reaction to be complete, and only one product was formed, which was identified as 2(2,2-dimethylvinyl)-1,3,5-triethylbenzene. The reaction mixture was decolourised by shaking with 100 ml of a 10 % solution of sodium sulphite and then with 50 ml of water. The organic phase was separated, dried (MgSO_4), the solvent evaporated and the oily residue, was chromatographed on a column of alumina with hexane as eluent. Evaporation of the solvent left 0.91 g of an oily colourless substance, which was pure according to GLC, yield 98 %. (Found: C 88.8; H 11.2. Calc. for $\text{C}_{16}\text{H}_{24}$: C 88.81; H 11.18). ^1H NMR (100 MHz CDCl_3): δ 1.26 (6H, t, CH_3 in ortho ethyls, $J = 7$ Hz), 1.45 (3H, t, CH_3 in para ethyl, $J = 7$ Hz), 1.63 (3H, d, cis- CH_3 to H in vinyl, $J = 0.2$ Hz), 2.17 (3H, d, trans- CH_3 to H in vinyl, $J = 0.5$ Hz), 2.83 (4H, m, CH_2 in ortho ethyls, $J = 7$ Hz), 2.99 (2H, q, CH_2 in para ethyl, $J = 7$ Hz), 6.91 (1H, m, CH, $J = 0.5$ Hz), 7.81 (2H, s, arom. H). IR (ν_{max} CCl_4): 3050 cm^{-1} (C-H str.), 1615 cm^{-1} (C=C str.). MS [m/e (%): 216 (65, M), 201 (100, $[\text{M}-\text{CH}_3]$), 187 (45, $[\text{M}-\text{C}_2\text{H}_5]$).

2,4,6-Trineopentylstyrene (37). The synthesis of this substance from 1,3,5-trineopentylbenzene has been published by Dahlberg *et al.*¹¹, and the published procedure was followed with the exception that iodine and copper oxide were used in the dehydration step. All spectroscopic data are in accordance with those published.

2-Acetyl-1,3,5-trimethylbenzene. This substance was prepared according to ref. 208. B.p. 125-126 $^{\circ}\text{C}/23$ torr, $n_{\text{D}}^{20} = 1.5176$. (Lit. b.p. 240 $^{\circ}\text{C}/735$ torr, $n_{\text{D}}^{20} = 1.5175$).²⁰⁸

2(1-Hydroxyethyl)-1,3,5-trimethylbenzene. This substance was prepared according to Klages *et al.*²⁰⁹; b.p. 140-141 $^{\circ}\text{C}/22$ torr. (Lit. b.p. 141 $^{\circ}\text{C}/24$ torr, 248 $^{\circ}\text{C}/760$ torr).²⁰⁹

2,4,6-Trimethylstyrene (Vinylmesitylene 35). This substance was prepared from 2(1-hydroxyethyl)-1,3,5-trimethylbenzene by the dehydration method described by Butenandt *et al.*²¹⁰; b.p. 86-87 °C/11 torr, $n_D^{25} = 1.5290$. (Lit. b.p. 92 °C/14 torr, $n_D^{25} = 1.5296$).²³⁴ ^1H NMR (CDCl_3): δ 2.22 (9H, s, CH_3), 5.20 (1H, q, CH trans to ring, $J = 16$ Hz), 5.48 (1H, q, CH cis to ring, $J = 12$ Hz), 6.69 (1H, q, CH=), 6.84 (2H, s, arom. H).

2,4,6-Triethylbenzaldehyde (42). The general procedure for the synthesis of mesitaldehyde (41) given in ref. 212 was followed, b.p. 91-92 °C/1 torr, $n_D^{25} = 1.5331$. (Lit. b.p. 146-149 °C/21 torr).²¹² ^1H NMR (CDCl_3): δ 1.23 (9H, t, CH_3 , $J = 7.5$ Hz), 2.62 (2H, q, CH_2 , $J = 7.5$ Hz), 2.95 (4H, q, CH_2 , $J = 7.5$ Hz), 6.92 (2H, s, arom. H), 10.54 (1H, s, CHO).

2,4,6-Triisopropylbenzaldehyde (43). 1,3,5-Triisopropylbenzene (15.0 g, 62.5 mmol) dissolved in 150 ml of methylene chloride was mixed with titanium tetrachloride (39.8 g, 212 mmol) and dichloromethyl methylether (15.0 g, 137 mmol) (prepared according to ref. 213) was added according to the procedure described by Bayer and Höft for the synthesis of mesitaldehyde (41).²¹⁴ The reaction was followed by GC 3 % SE 30 on Carbowax) and was found to be complete (99 % had reacted) after 12 h. After work up,²¹³ the product was distilled in vacuum to give 12.5 g, of an oil, yield 86 %, b.p. 96-97 °C/0.2-0.3 torr, $n_D^{21} = 1.5151$. (Lit. b.p. 85 °C/0.08 torr, $n_D^{20} = 1.5141$ -1.5150, b.p. 123-125 °C/4 torr).²¹⁴ ^1H NMR (CDCl_3): δ 1.00 (18H, d, CH_3 , $J = 7$ Hz), 2.64 (1H, m, CH, $J = 7$ Hz), 3.35 (2H, m, CH, $J = 7$ Hz), 6.90 (2H, s, arom. H), 10.42 (1H, s, CHO).

2,4,6-Trineopentylbenzaldehyde (44). This substance was prepared from 1,3,5-trineopentylbenzene by the method described for the synthesis of 2,4,6-triisopropylbenzaldehyde (43). After 40 h reaction time GC (3 % SE 30 on Carbowax) showed the reaction to be complete (99 % had reacted). The reaction mixture was hydrolysed with 40 ml of water, the organic phase separated and the aqueous phase extracted with two 25 ml portions of methylene chloride. The organic phases were combined, washed with 15 ml of a saturated solution of sodium chloride, 10 ml of water and dried (MgSO_4). The solvent was evaporated and the solid black residue was sublimated at 120-125 °C/0.08 torr, giving a white crystalline product, yield 96 %, m.p. 54-55 °C. (Found: C 83.3; H 11.7. Calc. for $\text{C}_{22}\text{H}_{36}\text{O}$: C 83.47; H 11.48). ^1H NMR (CDCl_3): δ 0.90 (18H, s, $\text{C}(\text{CH}_3)_3$), 0.92 (9H, s, $\text{C}(\text{CH}_3)_3$), 2.46 (2H, s, CH_2), 2.92 (4H, s, CH_2), 6.76 (2H, s, arom. H), 10.47 (1H, s, CHO). IR (ν_{max} CCl_4): 1695 cm^{-1} (C=O str.), 1400 cm^{-1} (C=C str.). MS [m/e (%): 316 (15, M), 301 (15, $[\text{M}-\text{CH}_3]$), 259 (13, $[\text{M}-\text{tBu}]$).

N-Methylbenzaldimine (45). The procedure of Kindler²¹⁵ was followed. Benzaldehyde (7.8 g, 73.5 mmol) was mixed with methylamine (11.9 ml, 270 mmol) in an autoclave which was heated to 85 °C for 5 h with agitation. The autoclave

was opened and the contents distilled, b.p. 90-91 °C/30 torr, $n_D^{23} = 1.5519$. (Lit. b.p. 90-91 °C/30 torr, $n_D^{20} = 1.5540$).²¹⁵

N-Methyl-2,4,6-trimethylbenzalimine (N-methylmesitaldimine 46). The general procedure for synthesis of compound (45) was followed. The reaction time was 15 h, yield 91 %, b.p. 118-119 °C/14 torr. (Found: C 83.3; H 8.33; N 8.66. Calc. for $C_{11}H_{13}N$: C 82.47; H 8.23; N 8.80). 1H NMR ($CDCl_3$): δ 2.22 (3H, s, CH_3), 2.34 (6H, s, CH_3), 3.47 (3H, s, $=NCH_3$), 6.73 (2H, s, arom. H), 8.53 (1H, s, $CH=N$). IR (ν_{max} CCl_4): 1645 cm^{-1} (C=N str.). MS [m/e (%): 161 (33, M), 146 (100, [M- CH_3]), 132 (37, [M-N CH_3]).

N-Methyl-2,4,6-triethylbenzalimine (47). The procedure for the synthesis of N-methylbenzalimine (45) was followed, yield 95 %, b.p. 92-93 °C/1 torr. (Found: C 82.3; H 10.4; N 6.57. Calc. for $C_{14}H_{21}N$: C 82.67; H 10.45; N 6.88). 1H NMR ($CDCl_3$): δ 1.14 (9H, m, CH_3 , J = 7 Hz), 2.66 (6H, m, CH_2 , J = 7 Hz), 3.84 (3H, s, NCH_3), 6.79 (2H, s, arom. H), 8.54 (1H, s, $N=CH$). IR (ν_{max} CCl_4): 1650 cm^{-1} (C=N str.). MS [m/e (%): 203 (21, M), 188 (100, [M- CH_3]), 174 (20, [M-N CH_3]).

N-Methyl-2,4,6-triisopropylbenzalimine (48). The procedure given for the synthesis of compound (45) was followed. The reaction time was 15 h at 95 °C, yield 98 %, b.p. 95-96 °C/0.2 torr. (Found: C 83.2; H 11.1; N 5.86. Calc. for $C_{17}H_{27}N$: C 83.17; H 11.10; N 5.73). 1H NMR ($CDCl_3$): δ 0.94 (12H, d, CH_3 , J = 7 Hz), 0.96 (6H, d, CH_3 , J = 7 Hz), 2.58 (1H, m, CH, J = 6-7 Hz), 2.97 (2H, m, CH, J = 7 Hz), 3.20 (3H, s, NCH_3), 6.67 (2H, s, arom. H), 8.31 (1H, s, $CH=N$). IR (ν_{max} CCl_4): 1655 cm^{-1} (C=N str.). MS [m/e (%): 245 (13, M), 230 (100, [M- CH_3]), 215 (27, [M-N CH_3]).

N-Methyl-2,4,6-trineopentylbenzalimine (49). The procedure described for the synthesis of compound (45) was followed. The reaction time was 20 h at 95 °C. After work up the product was chromatographed on a column of alumina with methylene chloride as eluent. Evaporation of the solvent left a white crystalline residue, yield 98 %, m.p. 56-57 °C. (Found: C 83.9; H 11.8; N 4.38. Calc. for $C_{23}H_{39}N$: C 83.83; H 11.93; N 4.24). 1H NMR ($CDCl_3$): δ 0.88 (18H, s, $C(CH_3)_3$), 0.95 (9H, s, $C(CH_3)_3$), 2.43 (2H, s, CH_2), 2.75 (4H, s, CH_2), 3.49 (3H, s, NCH_3), 6.74 (2H, s, arom. H), 8.52 (1H, s, $N=CH$). IR (ν_{max} CCl_4): 1690 cm^{-1} (C=N str.). MS [m/e (%): 329 (14, M), 314 (100, [M- CH_3]), 300 (7, [M-N CH_3]).

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